ADVANCES IN SYNTHESIS AND APPLICATION OF THE DERIVATIVES OF PORPHYRIN AS REAGENTS IN ANALYTICAL CHEMISTRY

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ABSTRACT

The derivatives of porphyrin have exhibited very high sensitivity as chromogenic reagents for determination of trace metal elements. Their sensitivity constitutes an obvious advantage over other reagents such as bisazo derivatives of arsenazo and phosphonazo. Therefore, their synthesis and application has attracted considerable attention. Up to now, over 80 derivatives of porphyrin have been reported in the literature as chromogenic reagents. In recent years, analysts have studied the influence of substituent groups on the analytical characteristics of the reagents, some novel reagents have been designed and synthesized, their properties, such as selectivity, reaction time and the acidity range, have been remarkably improved. Thus, they can be used to determine various metal elements in complex samples. Today, the derivatives of porphyrin have become increasingly important reagents in analytical chemistry. The present paper briefly reviews the synthesis of reagents, their structures and their analytical characteristics and application in analytical chemistry.

INTRODUCTION

The derivatives of porphyrin are reagents containing the porphyrin ring. The porphyrin ring contains sixteen different atoms; four nitrogen atoms form a special center of flexure. The center of flexure has a permanent spatial position and a strong coordination function. Because the geometrical configuration of the coordinate environment is very rigorous, only metal ions with a size and geometrical configuration equal to that of the porphyrin ring can enter and react with the reagent to form a stable complex. At present, the porphyrin reagents mainly used contain phenyl or other large ring substituents. This strongly increases the range of the π-electron conjugate system and obviously provides a better sensitivity than other analytical reagents, such as derivatives of arsenazo and phosphonazo. Their molar absorptivity often exceeds 10^5, being in some cases close to 10^6 or higher. Experiments have indicated that substituent groups and their positions in the

reagent structure influence the electron cloud density and the spatial steric hindrance of the coordinate environment; this may result in a change in the analytical characteristics of the reagents. Over 80 derivatives of porphyrin have been designed and synthesized by analysts and have been applied as chromogenic reagents for spectrophotometric determination of lead, zinc, copper and other heavy metal elements in real samples. In this paper, the analytical characteristics concerning the structure and the synthesis of the reagents, as well as their application, are reviewed.

THE SYNTHESIS OF THE PORPHYRIN REAGENT

The derivatives of porphyin have a similar structure (see Fig.1); all reagents contain a porphyrin ring, different reagent having different substituents (R_1, R_2, R_3 and R_4). If the four Rs are identical, the reagents are called symmetrical porphyrins, while others are called asymmetrical porphyrins. At present, the derivatives of porphyrin used in analytical chemistry are mainly symmetrical porphyrins. Moreover, the reagents also contain many different substituents in R; they influence the method of synthesis and the yield. Thus, reagents containing different substituents were often synthesized under different reaction conditions (see Table 1). In general, the derivatives of porphyrin are synthesized by reacting an aldehyde

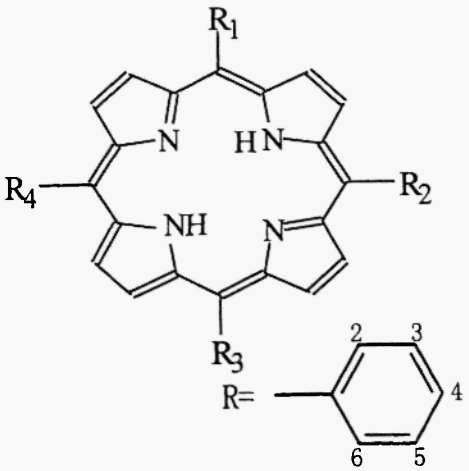
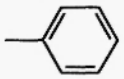
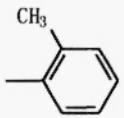
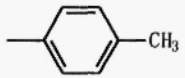


Fig. 1: The structures of porphyric reagents in which R is a benzene ring or other groups.

Table1

The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (phenyl)porphyrin (TPP)		Standard method Transfer equal molar quantities of pyrrole and benzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then heat and boil solution for 3 hours.	/1/ /2/
Meso-tetra (2-methyl-phenyl) porphyrin (T (2-MP)P)		Standard method	/3/
Meso-tetra (4-methyl-phenyl) porphyrin (T (4-MP)P)		Standard method Transfer equal molar quantities of pyrrole and p-methylbenzaldehyde dissolved in N, N-dimethyl-formamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then boil solution for 2 hours under heating.	/4/ /2/

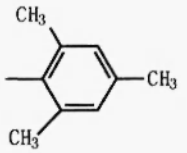
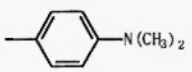
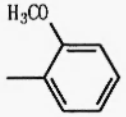
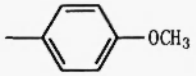
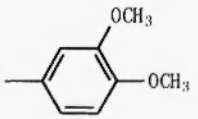
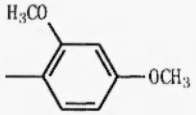
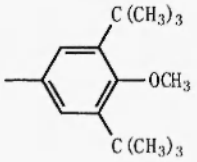
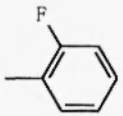
Meso-tetra (2, 4, 6-trimethylphenyl)porphyrin (T (2, 4, 6-TMP)P)		Dissolve equal molar quantities of pyrrole and 2, 4, 6-trimethyl-benzaldehyde in chloroform, add BF_3-ether to the solution, transfer the mixture into a distillation flask with a refluxing coil, then heat and maintain the solution boiling under nitrogen gas protection for 2 hours.	/5/
Meso-tetra (4-dimethylammonium-phenyl)-porphyrin (T (4-DMAP)P)		Dissolve equal molar quantities of pyrrole and N, N-dimethylamine-benzaldehyde in chloroform, add trifluoroacetic acid. Transfer the above mixture into a distillation flask with a refluxing coil, then heat and maintain the solution boiling under argon gas protection for 2hours.	/6/
Meso-tetra (2-methoxyl-phenyl)porphyrin (T (2-MOP)P)		Standard method	/3/
Meso-tetra (4-methoxyl-phenyl)porphyrin (T (4-MOP)P)		Standard method Transfer equal molar quantities of pyrrole and p-methoxylbenzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then heat and boil for 2 h.	/7/ /2/

Table1 (continued / 2)

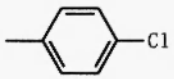
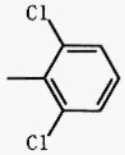
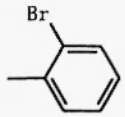
The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (3, 4-di methoxylphenyl)porphyrin (T (3, 4-DMOP)P)		Transfer equal molar quantities of pyrrole and 3, 4-dimethoxylbenzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then, heat and maintain solution boiling for 2 h.	/2/
Meso-tetra (2, 4-di-methoxylphenyl)porphrin (T (2, 4-DMOP)P)		Transfer equal molar quantities of pyrrole and 2, 4-dimethoxylbenzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then, heat and maintain solution boiling for 2 h.	/2/
Meso-tetra (3, 5-di tertiary- butyl-4-methoxylphenyl) porphyrin (T (DBMOP)P)		Dissolve equal molar quantities of pyrrole and 3, 5-ditertiary butyl-4-methoxylbenzaldehyde in chloroform, add BF_3-ether to the solution, transfer the mixture into a distillation flask with a refluxing coil, then heat and maintain the solution boiling under nitrogen gas protection for 2 hours.	/8/
Meso-tetra (2-fluoro-phenyl)porphyrin (T (2-FP)P)		Standard method	/3/

Meso-tetra (3-fluorin phenyl)porphyrin (T (3-FP)P)		Standard method	/9/
Meso-tetra (4-fluorin phenyl)porphyrin (T (4-FP)P)		Standard method Transfer equal molar quantities of pyrrole and 4-fluorinbenzaldehyde dissolved in N, N-dimethyl-formamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then heat and boil solution for 2 h.	/3/ /2/
Meso-tetra (2-chloro phenyl)porphyrin (T (2-ClP)P)		Standard method Transfer equal molar quantities of pyrrole and 2-chlorobenzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then heat and boil solution for 2 h.	/3/ /2/
Meso-tetra (3-chloro-phenyl)porphyrin (T (3-ClP)P)		Standard method	/10/

Table1 (continued / 3)

The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (4-chloro-phenyl)porphyrin (T (4-ClP)P)		Standard method.	/3/
		Transfer equal molar quantities of pyrrole and 4-chlorobenzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then heat and boil solution for 2 h.	/2/
Meso-tetra (2, 6-dichloro-phenyl)porphyrin (T (2, 6-DClP)P)		Transfer equal molar quantities of pyrrole and 2, 6-dichlorobenzaldehyde dissolved in benzene and acetic acid into a distillation flask with a refluxing coil, then heat and boil solution for 2 h.	/3/
Meso-tetra (2-bromo-phenyl)porphyrin (T (2-BrP)P)		Standard method	/3/

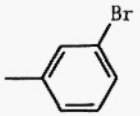
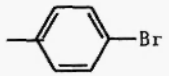
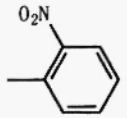
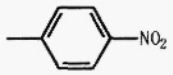
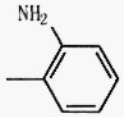
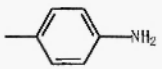
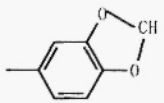
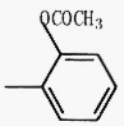
Meso-tetra (3-bromo-phenyl)porphyrin (T (3-BrP)P)		Standard method	/11/
Meso-tetra (4-bromo-phenyl)porphyrin (T (4-BrP)P)		Standard method.	/3/
		Dissolve equal molar quantities of pyrrole and 4-bromobenzaldehyde in N, N-dimethylformamide, add anhydrous aluminum chloride, transfer the mixture into a distillation flask with a refluxing coil, then heat and boil the solution for 2 h.	/2/
Meso-tetra (2-nitro-phenyl)porphyrin (T (2-NO_2P)P)		Dissolve equal molar quantities of pyrrole and 2-nitrylbenzaldehyde in acetic acid and acetic anhydride, transfer the mixture into a distillation flask with a refluxing coil, then maintain the solution boiling for 2 h.	/12/
		Standard method	/13/
Meso-tetra (4-nitro-phenyl)porphyrin (T (4-NO_2P)P)		Dissolve equal molar quantities of pyrrole and 4-nitrylbenzaldehyde in N, N-dimethylformamide, add anhydrous aluminum chloride, transfer the mixture into a distillation flask with a refluxing coil, then heat and main ain the solution boiling for 2 h.	/2/

Table1 (continued / 4)

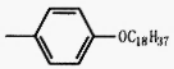
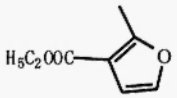
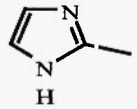
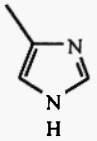
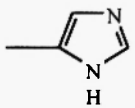
The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (2-amido-phenyl) porphyrin (T (2-NH_2P)P)		Dissolve T (2-NO_2P)P in concentrated HCl, add $SnCl_2$, then deposit the solution for 30min maintaining the reaction temperature between 65 and 70 °C. After that, neutralize the solution by adding NaOH, then extract the T (2-NH_2P)P with benzene.	/12/
Meso-tetra (4-amido-phenyl)porphyrin (T (4-NH_2P)P)		Dissolve equal molar quantities of pyrrole and 4-aminobenzaldehyde in N, N-dimethylformamide, add anhydrous aluminum chloride, transfer the mixture into a distillation flask with a refluxing coil, then heat and maintain the solution boiling for 2h.	/2/
Meso-tetra (3, 4-methinedioxylphenyl) porphyrin (T (MDOP)P)		Standard method.	/14/
Meso-tetra (2-acetoxy-phenyl)porphyrin (T (2-AOP)P)		Standard method	/15/

Meso-tetra (4-acetoxy-phenyl) porphyrin (T (4-AOP)P)		Standard method	/16/
Meso-tetra (2-acetaminophenyl)porphyrin (T (4-AAP)P)		T (4-NH_2P)P dissolved in acetone-ether reacts with acetyl chloride in the presence of pyridine	/17/
Meso-tetra (4-niacinamidephenyl)porphyrin (T (4-NAP)P)		Transfer T (4-NH_2P)P dissolved in dichloromethane, niacinamide and pyridine into a distillation flask with a refluxing coil, then heat and boil solution for 2 h.	/18/
Meso-tetra (4-pentoxyl-phenyl)porphyrin (T (4-C_5H_{11}OP)P		T (4-HP)P dissolved in DMF reacts with 1-bromopentane in the presence of K_2CO_3 at 80 °C for 3 hours.	/19/
Meso-tetra (4-octoxyl-phenyl)porphyrin (T (4-C_8H_{17}OP)P)		Standard method	/20/
Meso-tetra (4-dodecoxyl-phenyl)porphyrin (T (4-$C_{12}H_{25}$OP)P)		Standard method	/20/
Meso-tetra (4-cetoxyl-phenyl)porphyrin (T (4-$C_{16}H_{33}$OP)P)		The standard method	/20/

Table1 (continued / 5)

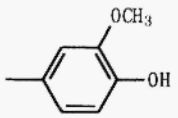
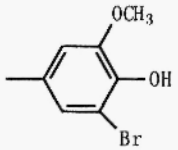
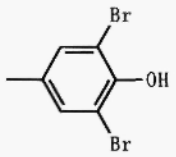
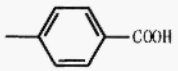
The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (4-octadecoxyl-phenyl)porphyrin (T (4-$C_{18}H_{37}$OP)P)		T (4-HP)P dissolved in DMF reacts with 1-iodinoctadecane in the presence of K_2CO_3 for 15 hours under N_2 protection.	/21/
Meso-tetra (3-acetoxy-2-furanyl) porphyrin (T ($FCOOC_2H_5$)P)		Transfer equal molar quantities of pyrrole and 3-acetoxy-2-furan-formaldehyde dissolved in acetic pyridine into a distillation flask with a refluxing coil, then heat and maintain solution boiling for 2 h.	/22/
Meso-tetra (2-imidazole) porphyrin (T (2-IP)P)		Standard method	/23/
Meso-tetra (4-imidazole) porphyrin (T (4-IP)P)		Standard method.	/23/
Meso- etra (5-imidazole) porphyrin (T (5-IP)P)		Standard method	/23/

Meso-tetra (3-pyridine) porphyrin (T (3-Py)P)		Standard method	/24/
Meso-tetra (4-pyridine) porphyrin (T (4-Py)P)		Standard method	/25/
Meso-tetra (2-hydroxyl-phenyl)porphyrin (T (2-HP)P)		Standard method	/26/
Meso-tetra (3-hydroxyl-phenyl)porphyrin (T (3-HP)P)		Standard method	/16/
Meso-tetra (4-hydroxyl-phenyl) porphyrin (T (4-HP)P)		Standard method Transfer equal molar quantities of pyrroie and 4-hydroxylbenzaldehyde dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, add anhydrous aluminum chloride, then heat and maintain solution boiling for 2 h.	/2/ /27/
Meso-tetra (3, 4-dihydroxyl-phenyl) porphyrin (T (3, 4-DHP)P)		Standard method	/16/

Table1 (continued / 6)

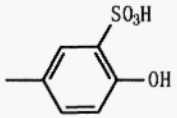
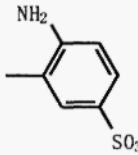
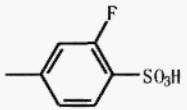
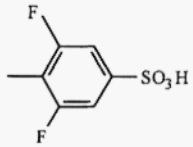
The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (3-methoxyl-4-hydroxyl -phenyl) porphyrin (T (3-MO-4-HP)P)		Transfer equal molar quantities of pyrrole and 3-methoxyl-4-hydroxy-benzaldehyde dissolved in acetic acid into a distillation flask with a refluxing coil, then heat and maintain solution boiling for 2 h.	/28/
Meso-tetra (3-methoxyl-5-bromo-4-hydroxyl-phenyl) porphyrin (T (3-MO-5-Br-4-HP)P)		Standard method	/29/
Meso-tetra (3, 5-dibromo-4-hydroxyl -phenyl) porphyrin (T (DBHP)P)		Standard method	/30/
Meso-tetra (4-carboxyl-phenyl) porphyrin (T (4-CP)P)		Standard method	/31/

Meso-tetra (4-methyl-3-sulfonphenyl) porphyrin (T (4-M-3-SP)P)		T (4-MP)P reacts with 15% H_2SO_4 at a temperature between 100 and 120 °C for 45min.	/32/
Meso-tetra (4-isopropyl- 3-sulfonphenyl)porphyrin (T (4-I-3-SP) P)		TPP dissolved in $CHCl_3$ reacts with chlorosulfonic acid for 40min at a temperature between 25 and 40 °C	/33/
Meso-tetra (4-benzene sulfonic phenyl)porphyrin (TSBP)		TBP reacts with concentrated H_2SO_4.	/33/
Meso-tetra (2-naphthalene sulfonic acid)porphyrin (TS (2-N)P)		TNPP reacts with concentrated H_2SO_4.	/33/
Meso-tetra (4-methoxyl-3-sulfonphenyl)porphyin (T (4-MOSP)P)		T (4-MOP)P reacts with 10%H_2SO_4.	/34/
Meso-tetra (2-hydroxyl-5-sulfonphenyl)porphyrin (T (2-H-5-SP)P)		T (2-HP)P reacts with 98% H_2SO_4	/26/

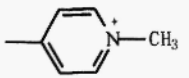
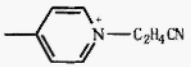
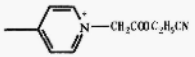
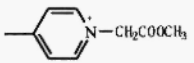
Table 1 (continued / 7)

The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (4-hydroxyl-5-sulfonphenyl)porphyrin (T (4-H-3-SP)P)		T (4-HP)P reacts with 98% H_2SO_4	/35/
Meso-tetra (2-amido-5-sulfonphenyl)porphyrin (T (2-NH_2-5-SP)P)		T (2-NH_2P)P reacts with concentrated H_2SO_4 for 4 h at a temperature between 120 and 140 °C	/12/
Meso-tetra (3-fluorin-4-sulfonphenyl) porphyrin (m-FTPPS$_4$)		T (3-FP)P reacts with concentrated H_2SO_4 for 4 h at a temperature between 120 and 140 °C	/9/
Meso-tetra (2, 6-difluoro-4-sulfonphenyl)porphyrin (T (2, 6-DFSP)P)		T (2, 6-DFP)P reacts with H_2SO_4.	/33/

Meso-tetra (3-chloro-4-sulfonphenyl)porphyrin (m-ClTPrS$_4$)		T (3-ClP)P reacts with 25% H_2SO_4 for 1hour at 120 °C.	/10/
Meso-tetra (3-bromo-4-sulfonphenyl)porphyrin (m-BrTPPS$_4$)		T (3-BrP)P reacts with 30% H_2SO_4 for 1 h at 120°C.	/3/
Meso-tetra (5-sulfon-thienyl)porphyrin (T (5-STP)		TSTP reacts with concentrated H_2SO_4 at 85°C	/36/
Meso-tetra (4-trime hyl-aminophenyl)porphyrin (T (4-TMAP)P)		T (4-DMAP)P reacts with CH_3I for 30min.	/37/
Meso-tetra (N-methyl-3-pyridyl)porphyrin (T (3-MPy)P)		T (3-Py)P reacts with p-methyl-methyl benzenesulfonate in a chloroform solution.	/38/
Meso-tetra (4-N-nitrile-cymenepyridyl)porphyrin (T (pNACNPy)P)		T (4-Py)P and bromide methylnitrile reflux in $CHCl_3$ for 24 hours.	/39/

Table1 (continued / 8)
The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The me hod of synthesis of reagents	Ref.
Meso-tetra (N-methyl-4-pyridyl)porphyrin (T (4-MPy)P)		T (4-Py)P reacts with p-methyl-methyl benzenesulfonate in a DMF solution.	/40/
Meso-tetra (4-N-nitrile-ethylpyridyl)porphyrin (T (rNPCNPy)P)		T (4-Py)P and bromide ethyl-nitrile reflux in $CHCl_3$ for 36 hours.	/39/
Meso-tetra (4-N-ethoxy-carboxylmethylpyridyl) porphyrin (T (rNEAEsPy)P)		T (4-Py)P and bromide acetic acid ethyl ester reflux in $CHCl_3$ for 6 hours	/39/
Meso-tetra (4-N-methoxy-carboxylmethylpyridyl) porphyrin (T (rNEAMsPy)P)		T (4-Py)P and chloride acetic acid methyl ester reflux in $CHCl_3$ for 10 hours.	/39/

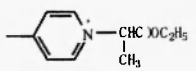
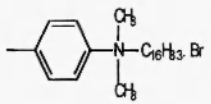
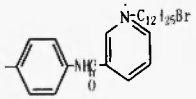
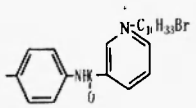
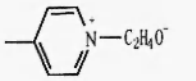
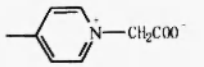
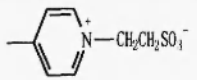
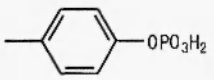
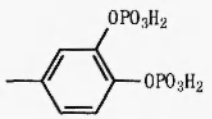
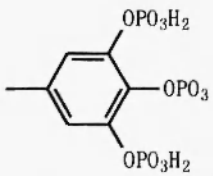
Meso-tetra (4-N- (1-methyl ethoxyl-methyl-carboxyl)-pyridyl) porphyrin (TrNPAEsPy)P)		T (4-Py)P and dibromide propionic acid ethyl ester reflux in $CHCl_3$ for 20 hours.	/39/
Bromide meso-tetra (4-N, N, N-dimethyl-hexadecyl-amino-phenyl) porphyrin (TDMHAPP)		Transfer T (4-DMAP)P and bromo-cetane dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, then heat and boil solution for 2 h under N_2 protection.	/41/
Bromide meso-tetra (4-dodecylniaciamidephenyl) porphyrin (TDNAPP)		Transfer TNAPP and bromide dodecane dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, then heat and boil solution for 2 h under N_2 protection.	/42/
Bromide meso-tetra (4 hexadecylniaciamide phenyl)porphyrin (THNAPP)		Transfer TNAPP and bromide cetane dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, then heat and boil solution boiling for 2 h under N_2 protection.	/42/
Meso-tetra (1-pyridyl-ethoxyl)porphyrin (T (4-HEPy)P)		Transfer T (4-Py)P and 2-bromoethanol dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, then heat and boil solution for 10 h	/43/
Meso-tetra (1-pyridyl-carboxyethyl)porphyrin (T (4-CMPy)P)		Transfer T (4-Py)P and 2-chloroacetic acid dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, then heat and boil solution for 10 h	/43/

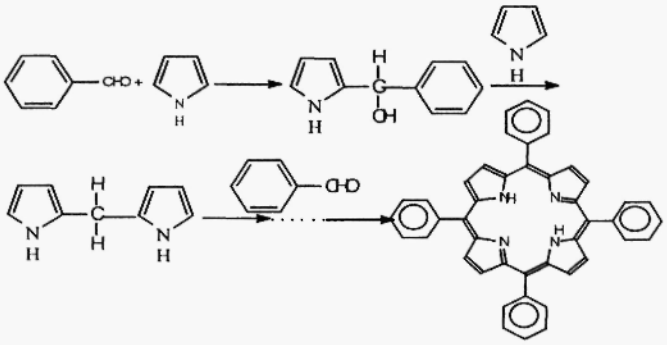
Table1 (continued / 11)

The synthesis of porphyrin reagents

Reagent	$R_1=R_2=R_3=R_4$	[a] The method of synthesis of reagents	Ref.
Meso-tetra (1-pyridyl-2-sulfonic acid ethyl) porphyrin (T (4-SEPy)P)		Transfer T (4-Py)P and 2-bromoethane sulfonic acid dissolved in N, N-dimethylformamide into a distillation flask with a refluxing coil, then heat and boil solution for 10 h.	/43/
Meso-tetra (4-phosphonoxylphenyl)porphyrin ($TPPP_n$)		T (4-HP)P reacts with pyrophosphoric acid and P_2O_5	/44/
Meso-tetra (3, 4-diphosphonoxylphenyl) porphyrin ($TPPP_d$)		T (3, 4-DHP)P reacts with pyrophosphoric acid and P_2O_5	/44/
Meso-tetra (3, 4, 5-triphosphonoxylphenyl) porphyrin ($TPPP_t$)		T (3, 4, 5-THP)P reacts with pyrophosphoric acid and P_2O_5	/44/

[a] Standard method is as follows: Transfer equal molar quantities of pyrrole and corresponding aldehyde dissolved in propionic acid into a distillation flask with a refluxing coil, then heat the solution and maintain boiling for 1.0 hours.

with pyrrole under activation and heating. The suggested reaction mechanism was as follows:



The above procedure shows that the synthesis mechanism is complex; moreover, both pyrrole and aldehyde easily polymerize and, therefore, the synthesis and purification of derivatives of porphyrin have been a problem in organic and analytical chemistry for a very long time. This has influenced the application of the reagents in analytical chemistry. In recent years, the synthesis technology has remarkably improved various organic acids, such as propionic acid and butyric acid, BF_3-ether and $AlCl_3$, etc., have been suggested as activators in the literature /1-44/; the yield and purity of the reagent has been enhanced and the reaction conditions have become very simple and increasingly stable; usually, the selection of the activator and the other reaction conditions depends on the properties of the aldehyde, the main intention being to increase the activity of the aldehyde and avoid polymerisation of the pyrrole itself. Today, a maximum yield of 50-60% has been reported in the literature. A review of the synthesis of porphyrin compounds as spectrophotometric chromogenic reagents is given in Table1.

THE STRUCTURES AND THEIR ANALYTICAL CHARACTERISTICS

In the derivatives of the porphyrin molecule, the porphyrin ring is a functional group, and R_1, R_2, R_3 and R_4 act as auxochromes. Being electron effective, reagents containing different Rs obviously have different chemical properties. Moreover, the substituents and their positions may remarkably influence the analytical characteristics of derivatives of porphyrin in R by an

electronic effect. Therefore, the design of the molecules is an important task in obtaining good sensitivity and selectivity. This has been used largely and some excellent porphyrin compounds have been synthesized on the basis of the above law. This easily resolved the problems of porphyrin reagent sensitivity and selectivity. Certainly, the selection of optimal reaction conditions is also very important in improving sensitivity and selectivity. For example, the activator and heating can speed up the reaction rate remarkably; it is used widely in spectrophotometric determination of various trace metal elements. In general, the derivatives of porphyrin as analytical reagents possess remarkable characteristics in the following respects:

1. Sensitivity

The influence of the substituent groups and positions on the sensitivity is complex; there is always a difference between different metal elements. For copper, reagents containing hydroxyl and methylammonium have a higher sensitivity than other reagents, such as reagents containing a nitro group, when the substituent groups are the same, the reagents containing p-position or o-position substituent groups have a higher sensitivity than the m-position (see Table 2). Otherwise, the above law cannot be fully applied to other metal elements. In general, high sensitivity is a remarkable characteristic of the derivatives of porphyrin; it can be applied to the spectrophotometric determination of metal elements in very low concentration samples; ppb concentrations can usually be determined without preconcentration or condensed sample solutions. Super-high sensitive chromogenic reaction has been reported in the literature in recent years (see Table 3), which shows that the sensitivity of a porphyrin compound can be greatly enhanced.

2:Absorption spectra

A porphyrin compound is a polybasic acid. The porphyrin ring may dissociate according to the following formula in an aqueous solution (in order to simplify, the porphyrin ring was replaced by H_2P):

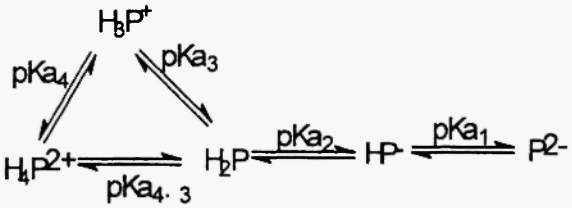


Table 2
Comparison of the sensitivities of the reactions of copper with derivatives of porphyrin

Reagent		Molar absorptivity
Meso-tetraphenylporphyrin	TPP	4.76×10^5
Meso-tetra (4-sulfophenyl)porphyrin	T (4-SP)P	3.7×10^5
Meso-tetra (4-carboxylphenyl)-porphyrin	T (4-CP)P	4.2×10^5
Meso-tetra (3-N-methylpyridyl)-porphyrin	T (3-MPy)P	4.0×10^5
Meso-tetra (4-N-methylpyridyl)-porphyrin	T (4-MPy)P	2.46×10^5
Meso-tetra (5-sulfonthienyl)-porphyrin	T (5-ST)P	2.98×10^5
Meso-tetra (4-hydroxylphenyl)-porphyrin	T (4-HP)P	3.18×10^6
Meso-tetra (4-dimethylammonium-phenyl) porphyrin	T (4-DMAP)P	3.9×10^6
Meso-tetra (ethoxy-carboxylfuran)-porphyrin	$TF_{COOC2H5}P$)	1.52×10^5
Meso-tetra (3-F-4-sulfonphenyl)-porphyrin	m-$FTPPS_4$	4.4×10^5
Meso-tetra (3-Br-4-sulfonphenyl)-porphyrin	m-$BrTPPS_4$	2.38×10^5
Meso-tetra (2-CI-4-sulfonphenyl)-porphyrin	o-$ClTPPS_4$	4.02×10^5
Meso-tetra (2-Br-4-sulfonphenyl)-porphyrin	o-$BrTPPS_4$	2.38×10^5
Meso-tetra (4-methoxylphenyl)-porphyrin	T(4-MO-3-SP)P	3.18×10^5
Meso-tetra (3-Br-4-hydroxyl-5-methoxyl-phenyl) porphyrin	T(3-Br-4-H-5-MOP)P	2.61×10^5
Meso-tetra (4-methoxylphenyl-3-sulfonic acid) porphyrin	T (4-MO-3SP)P	3.7×10^5
Meso-tetra (3-Br-4-sulfonphenyl)-porphyrin	T (3-Br-4-SP)P	2.61×10^5
Meso-tetra (4-trimethylammonium-phenyl)porphyrin	T (4-TMAP)P	1.0×10^7
Meso-tetra (4-methoxylphenyl)-porphyrin	T (4-MOP)P)	3.39×10^5

Table 3

Review of super high sensitivity chromogenic reaction of porphyrin reagents with metal ions

Reagent		Element	Molar absorptivity
Meso-tetra (4-dimethylammoniumphenyl)porphyrin	T (4-DMAP)P	Cu	3.9×10^5
Meso-tetra (2-hydroxyl-5- sulfophenyl)porphyrin	T (2-HP)PS4	Mn	6.4×10^5
Meso-tetra (4-hydroxylphenyl)porphyrin	T (4-HP)P	Pd	1.46×10^6
Meso-tetra (4-acetoxyphenyl)porphyrin	T (4-AOP)P	Ru	7.0×10^5
Meso-tetra (4-dimethylammoniumphenyl)porphyrin	T (4-DMAP)P	Pd	5.6×10^5
Meso-tetra (4-chlorphenyl)porphyrin	T (4-ClP)P	Co	7.94×10^5
Meso-tetra (4-acetoxyphenyl)porphyrin	T (4-AOP)P	Au	1.62×10^6
Meos-tetra (4-N-trimethylphenyl)porphyrin	T (TMAP)P	Cu	1.0×10^7
Meso-tetra (4-N-trimethylaminophenyl) porphyrin	T (4-TMAP)P	Mn	2.6×10^5
Meso-tetra (4-methyl-3-sulfophenyl)porphyrin	T (4-M-3-SP)P	Cd	7.6×10^5
Meso-tetra (4-acetoxyphenyl)porphyrin	T (4-AOP)P	Ir	1.36×10^6
Meso-tetra (3-bromo-4-hydroxyl-5-methoxylphenyl)porphyrin	T (3-Br-4-H-5-MOP)P	Zn	9.6×10^5
Meso-tetra (4-hydroxylphenyl)porphyrin	T (4-HP)P	Cu	3.18×10^6

The dissociation of a proton in the substituents of the reagent was not included in the above formula. In fact, substituents and their positions affect the dissociation of the porphyrin ring; some reagents' dissociation constants are listed in Table 4. Thus, a reagent with a different molecular structure has a different absorption spectrum (see Fig. 2 and Fig. 3).

Table 4
Dissociation in water of some porphyrin reagents

Reagent	pKa4	pKa3	pKa4. 3	pka2	pka1
T (4-CP)P			2. 1		
T (4-SP)P			4. 6		
T (3-MPy)P			2. 8		
T (4-HP)P	5. 4	5. 45			
T (4-MPy)P	0. 8	2. 06	2. 2	19. 2	16

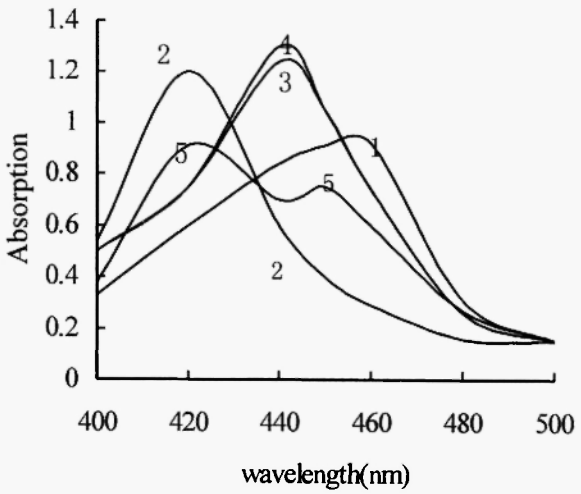


Fig. 2: The absorption spectrum of T(DBHP)P for different degrees of acidity: (1) 2.0 mol.l^{-1} HCl, (2) HCl-KCl buffer solution (pH=1), (3) 0.08 mol.l^{-1} NaOH solution, (4) 1.0 mol.l^{-1} NaOH, (5) 0.5 mol.l^{-1} HCl.

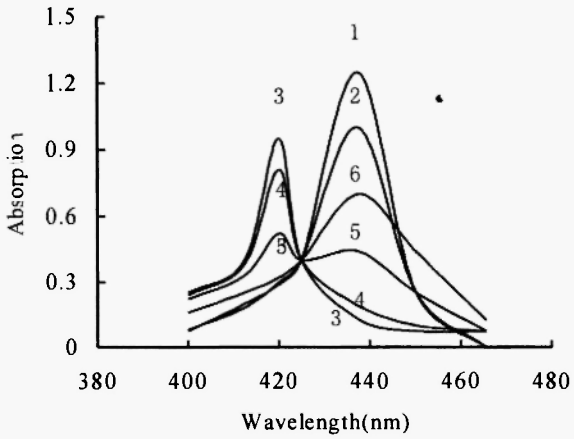


Fig. 3: The absorption spectra of T(3-MPy)P in solutions of different acidity: (1) 0.5 mol.l^{-1} HCl, (2) 1.0 mol.l^{-1} HCl, (3) pH = 7.0 buffer solution, (4) pH = 12.6 buffer solution, (5) pH = 13.08 buffer solution, (6) 1.0 mol.l^{-1} NaqOH solution.

The metal ions can often react with derivatives of porphyrin to form a very stable complex with a very sensitive "Soret" absorption band (400-500nm) (see Fig. 4). Both the reagent and its complex have a serious contiguous absorption spectrum, although the wavelength difference ($\Delta\lambda$) of the absorption peak is different with respect to different reagents and different metal ions, and some reactions' $\Delta\lambda$ are large, such as the complex of lead-porphyrin reagents; most of the reactions have small $\Delta\lambda$. Among these, , some are almost equal to zero. Because a large $\Delta\lambda$ is beneficial in improving the precision and accuracy of the determination method, three effective technologies have been widely used in the spectrophotometric determination of trace elements in the literature.

(1)Enhancing acidity after complex formation

If the complex is very stable in a highly acidic medium, enhancing the acidity of the system after complex formation can obviously increase, as the porphyrin reagent has different absorption spectra in solutions of different acidity (see Fig. 2 and Fig. 3). For example, when the acidity of a reaction system is at pH=5. 2, both Cu-$TPPS_3$ and $TPPS_3$ have almost the same absorption peak at 413nm, $\Delta\lambda$ is zero, it is difficult to determine copper precisely and accurately in real samples. Otherwise, after the reaction of

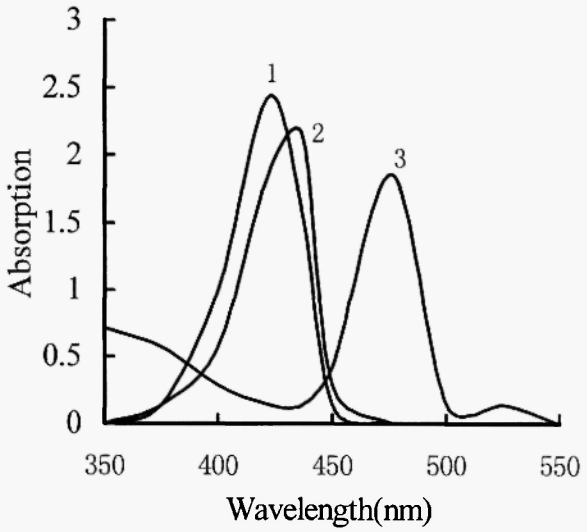


Fig. 4: Absorption spectra of Pb and Zn complexes: (1) T(4MPy)P against water, (2) Zn-T(4-MPy)P complex against reagent blank, (3) Pb-T(4-MPy)P against water. Other conditions: pH = 9.2.

$TPPS_3$ with copper is completed, chloroactic acid was added to the system (pH change from 5. 2 to 2. 0); this resulted in the $TPPS_3$'s protonation, he absorption peak of the reagent converted to 434nm; thus, $\Delta\lambda$ of the color system increased to 21 nm (see Fig. 5).

(2)Changing the surplus reagent in the system into a stable metal complex

After the color reaction of the metal ion (M_1), the reagent is finished, the surplus color reagent is changed completely into a stable complex by adding by adding a considerable amount of metal ion (M_2); if the stability constant of the M_2 complex is remarkably smaller than that of the M_1 complex, and larger than that of the other metal complex which interferes with M_1 that reacts with the reagent under the same conditions, this can increase $\Delta\lambda$ of the color reaction system and also improve the selectivity of the color reaction. For example, at pH = 9.2 T(4-MPy)P can react with zinc sensitively to form a stable zinc complex with an absorption peak at 437 nm, the wavelength difference between Zn-T (4-MPy)P and T(4-MPy)P is 15 nm after the reaction of zinc with T(4-MPy)P is completed. Adding a considerable

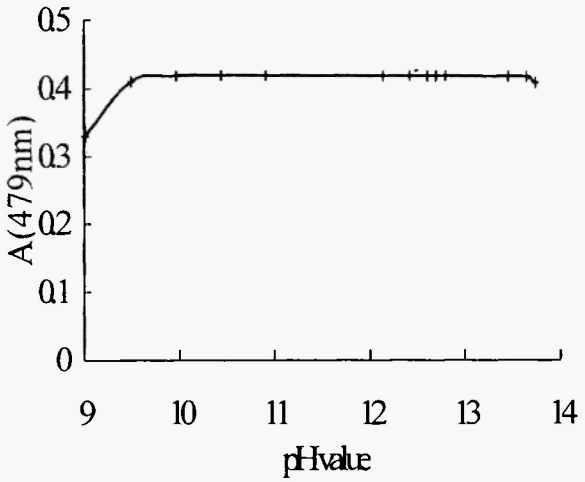


Fig. 5: The effect of acidity on the reaction of T(DBHP)P with lead (10 μg of lead)

amount of lead (II) to the system changed surplus T(4-MPy)P into a Pb-T(4-MPy)P complex with an absorption peak at 479 nm, so that $\Delta\lambda$ was enhanced to 39 nm (see Fig. 6). The method has been used widely for the spectrophotometric determination of trace metal ions.

(3) Extraction with organic solvents

If the solubility of the reagents and their metal complexes exhibit remarkable differences, the complexes can be extracted into an organic phase with a special organic solvent after the completion of the reaction of the metal ion with the reagent. This can remove the interference of the reagent in the determination and largely improve the selectivity. For example, T(3-MPy)P or T(4-MPy)P were used to determine trace copper; the copper complex was extracted into an organic phase with benzene and 2-nitro-propane, then copper was detected in the organic phase; the method showed good precision and accuracy.

3. Acidity of reaction

In general, the acidity obviously influences the color reactions of derivatives of porphyrin with metal ions; most of the reactions require serious

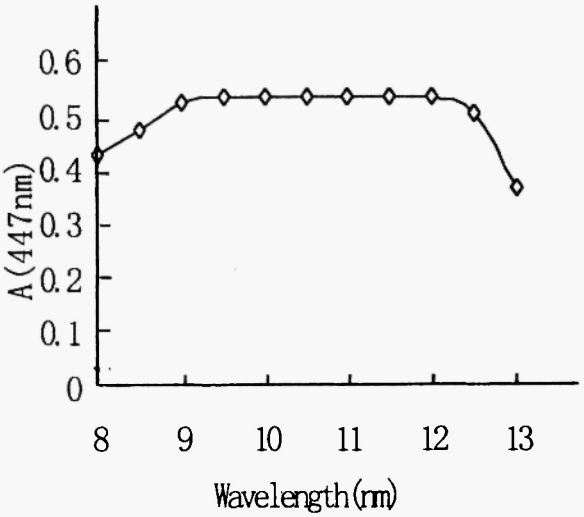


Fig. 6: The effect of acidity on the reaction of T(DBHP)P with zinc (5.0 μg of zinc).

Table 5

Effect of acidity on the reaction of porphyrin reagents with metal ions

Reaction (reagent/metal)	Reaction time (pH)
T (3-MPy)P/Cu	3min. at 100°C (4. 0);30min. at 100°C (2. 5)
T (3-MPy)P/Pb	1. 0min. at room temperature (10. 2);5. 0min. at room temperature (<10. 2)
T (4TMAP)P/Zn	7min. at 100°C (>4. 0);>7. 0min. at 100°C (<4. 0)
T (4-SP)P/Cu	10min. at 100°C (3. 6); 60min. at 100°C (2. 6)
T (4-SP)P/Pd	10min. at 100°C (3. 5) ; 60min. at 100°C (2. 6)
T (4-CP)P/Cu	2min. at 100°C (5. 9) ; 15min. at 100°C (4. 9)
TPP/Cu	2min. at 100°C (5. 5) ; 30min. at 100°C (3. 5)

control of the acidity. Meanwhile, acidity also affects reaction rate and analytical characteristics, such as sensitivity or selectivity. In recent years, analysts have found that some electron-withdrawing groups introduced into the benzene ring of R in the porphyrin ring can effectively increase the acidity range of the reaction. For example, T(DBHP)P, in which two bromides were added to the m-positions of the benzene ring of the reagent, reacts with lead(II) and zinc in a wide pH range (see Fig. 5 and Fig. 6). This indicated that the structure of derivatives of porphyrin reagents directly influences acidity and the acidity range of the reaction.

4. Selectivity

In the past, poor selectivity often existed in the reaction of metal with porphyrin reagents. The main interference elements are transition metals, which seriously affected the application of porphyrin compounds in complex samples, such as rock, steel and geochemical samples; they were only used for some simple cases, such as metal, reagents, sea water, river water, tap water, blood slum, hair and tea leaves, etc. Therefore, improving the selectivity of reactions will be an important task for analysts in the future. The following methods have been considered and used:

(1) Design of new porphyrin reagents

Table 6 shows that certain substituents introduced into the reagent may improve the selectivity remarkably, T (DBHP)P is a very successful example. Analysts should continue to study the law of the effect of substituents and their position in the R groups on the analytical characteristics of reagents and design and synthesize a set of highly selective and sensitive derivatives of porphyrin; this is an important method to increase selectivity.

(2) Selection of suitable activators

It was found that certain activators can speed up the velocity of the reaction of a metal ion with reagents selectively, so that the metal element reacts with the reagent rapidly and the reaction of coexisting elements with the reagent is also very slow; the difference in reaction rate can be used for determination of trace compounds and for avoidance of coexisting elements' interference. Some activator reactions published are listed in Table 7.

Table 6

Comparison of the selectivities of the reactions of lead with certain porphyrin reagents

Reagent	Tolerance amounts of foreign ion (μg)						
	Cr (III)	Fe (III)	Co (II)	Ni (II)	Cu (II)	Zn (II)	Cd (II)
$TPPS_3$	<1	<1		<1	<1	<1	<1
T (3-MPy)P	8	5	10	10	12	20	12
T (4-MAP)P	<5	<5	<5	<5	<5	<5	<5
T (4HP)P	<1	<1	10	10	5	<5	10
m-FTPPS$_4$	<1	10	<1	<1	<1	<1	<1
m-ClTPPS$_4$	<1	10	<1	<1	<1	<1	<1
m-BrTPPS$_4$	<1	10	<1	<1	<1	<1	<1
o-ClTPPS$_4$	<1	10	<1	<1	<1	<1	<1
o-BrTPPS$_4$	<1	10	<1	<1	<1	<1	<1
$TPPS_4$	<1	10	5	<1	<1	5	<1
T (4-MO-3-SP)P	1.0	1.0	6	1.0	40	5.0	4
T (2-HP)P	0.1	0.1	0.5	1	1	0.1	2
T (3-HP)P	0.1	0.1	0.5	1	1	0.1	2
T (3, 4-DHP)P	0.1	0.1	0.5	1	1	0.1	2
T (4-MOP)P	0.9	5	0.9	2	3	5	5
T (DBHP)P	1000	350	450	1000	550	2000	1000

Table7

The effect of activators on the reaction velocity of porphyrin with metal ions

The reaction (reagent/metal ion)	Activators	Reaction time (without activator)
T (4-TMAP)P/Cu	Oxammonium hydrochloride	5min. at room temperature (20min. at room temperature)
T (4-SP)P/Cd	Pyridine, γ-methylpyridine, imidazole	10min. at room temperature (45min. at room temperature)
T (4-SP)P/Pd	Ascorbic acid	8min. at 100°C (15min. at 100°C)
T (4-MPy)P/Mg	8-hydroxyquinoline	60min. at100°C (180min. at 100°C)
T (3-MPy)P/Cu	Oxammonium hydrochloride + Ascorbic acid+ sodium sulfite	2. 0min. at room temperature (10min. at100°C)
T (4-TMAP)P/Zn	7-iodo-5-sulfon-8-hydroxyl-quinoline	5. 0min. at room temperature (7min. at100°C)
$TPPS_3Cd$	dipyridine	4min. at room temperature (the reaction velocity is very slow at room temperature)
T (4-CP)P/Cd	Pyridine, γ-methylpyridine, imidazole	The reaction complete rapidly at room temperature (the reaction velocity is very slow at room temperature)
TPP/Fe (II)	Ascorbic acid	2. 5hour at100°C (the reaction velocity is very slow at room temperature)

(3)Selection of strongly acidic medium and exchange reaction

As the complexes are very stable in various acidic media, analysts always select a strongly acidic solution as a reaction medium. In strong acidity, metal complexes can also remain stable, and coexisting element complexes are decomposed; this is beneficial for improving the selectivity For example, 0.24 $mol.l^{-1}$ H_2SO_4 was selected as a medium of reaction of T(4-TMAP)P with copper; the complex of coexisting elements, such as zinc, reacts with (4-TMAP)P, decomposing immediately; this increases the selectivity of copper determination.

Exchange reaction is also an effective method of improving the selectivity. After the color reaction is completed, if another masking agent is added to the system, as the masking agent can react with coexisting ions to a very stable complex and decompose its porphyrin-complex, the metal complex is kept stable as it cannot react with the masking agent to form a stable compound. For example, after the reaction of T(4-SP)P with cobalt and cadmium is completed, the interference of cadmium can be easily removed by adding the masking agent EDTA.

(4)The separation

When the above methods are unable to resolve interference of coexisting elements, a suitable separation step should be adopted in determination of a trace metal element in complex samples.

5. Activators and Surfactants

The rate of the reaction of porphyrin reagents with lead, zinc and copper etc. is usually very slow; therefore, the reaction is carried out under heating conditions. In order to speed up the rate at room temperature, analysts have tested various organic reagents and metal ions; the results showed that certain compounds have a noticeable catalytic effect on the reaction of porphyrin with certain metal ions. This reduces reaction time, so that some reactions can be completed rapidly room temperature (see Table 7).

Two main catalytic mechanisms were reported in the literature:

(1): The activator reacts with metal to form an intermediate compound

For example, the reaction of lead with T (DBHP)P in NaOH medium (for the sake of simplicity) HQ substitutes 8-hydroxyquinoline and H_2P substitutes T (DBHP)P):

$$\begin{cases} a: Pb^{2+} + NaOH \longrightarrow Pb(OH)_4^{2-} + HQ \longrightarrow PbQ^{+} \text{ or } PbQ_2 + 2P^{2-} \longrightarrow PbP_2 \\ b: Pb^{2+} + NaOH \longrightarrow Pb(OH)_4^{2-} + 2P^{2-} \longrightarrow PbP_2 \end{cases}$$

In NaOH medium, lead formed $Pb(OH)_4^{2-}$, as both $Pb(OH)_4^{2-}$ and P^{2-} have a negative charge, and the static repulsion makes it difficult for them to close each other, so the chromogenic reaction almost does not take place at room temperature. Only under heating do $Pb(OH)_4^{2-}$ and P^{2-} get enough energy to collide and allow the color reaction to take place. In the presence of 8-hydroxyl-quinoline (a), as $Pb(OH)_4^{2-}$ has changed to PbQ^{+} or PbQ_2, which has a positive or a neutral charge, and the static attraction causes P^{2-} and PbQ^{+} or PbQ_2 to close each other, the chromogenic reaction takes place easily at room temperature.

(2)Exchange reactions

For example, the reaction of zinc with T (DBHP)P in a borax buffer solution (pH=10) (for the sake of simplicity ID substitutes imidazole, and H_2P substitutes T (DBHP)P):

$$\begin{cases} c: Zn^{2+} + 4OH^{-} \longrightarrow Zn(OH)_4^{2-} + P^{2-} \xrightarrow{slow} ZnP \\ d: Cd^{2+} + 4OH^{-} \longrightarrow Cd(OH)_4^{2-} + P^{2-} \xrightarrow{rapid} CdP \end{cases}$$
$$Zn(OH)_4^{2-} + ID \longrightarrow ZnID \text{ or } ZnID_2 + CdP \xrightarrow{rapid} ZnP$$

In a borax medium of pH=10, Zn^{2+} forms $Zn(OH)_4^{2-}$, H_2P forms P^{2-} ion, as both $Zn(OH)_4^{2-}$-and P^{2-} (c) have a negative charge, static repulsion to causes them to remain apart so that the color reaction does not to take place readily at room temperature. Only on heating have $Zn(OH)_4^{2-}$-and P^{2-} enough energy to collide and yield the color reaction. In the presence of Cd (II) and imidazole, as $Zn(OH)_4^{2-}$ (d) is converted into $ZnID^{+}$ or $ZnID_2$, and P^{2-}into CdP, which have a positive charge $ZnID^{+}$ or are neutral Zn ID_2, CdL, they approach easily to react chemically with each other. CdL is very unstable, it can be transformed into a very stable ZnP complex.

For reactions of porphyrin reagents with metal ions, various surfactants have been widely used. The surfactant has two functions: one is increasing the water solubility of the porphyrin reagent and its complexes, as many reagents are difficult to dissolve in water; even water-soluble porphyrin always shows poor solubility in a highly acidic medium. On the other hand, surfactants were selected to increase the sensitivity of the reaction. Experiments show that different surfactants have different effects, therefore,

the choice of surfactant should be based on the experimental results. For example, although both BHPP and its complex have good water solubility in an alkaline medium, the sensitivity of the complex without surfactants is very low. In order to enhance the sensitivity, the effect of surfactants on the reaction system was examined in detail; it was found that different types of surfactants exhibited different effects on the absorbance from the system (see Fig. 7). The results indicated that anionic surfactants, such as sodium dodecyl sulfate, do not influence to any considerable extent the absorbance of surfactants. Non-ionic surfactants, such as Tween-80, AEO-9 and TritonX-100, and cationic surfactants, such as CTMAB, clearly increased the absorbance of the complex. Since CTMAB gave smaller absorbance increments than non-sufactants, and TritonX-100 gave the highest sensitivity and low background signals, TritonX-100 was chosen.

APPLICATION IN ANALYSIS

Derivatives of porphyrin have been used extensively in analytical chemistry. At present, the main elements determined are copper, zinc, lead cadmium, palladium and manganese. It was found that different elements show different analytical characteristics as they react with porphyrin reagents. In general, porphyrin reagents can react with copper very sensitively; among thesis, T (4-DMAP)P, T (4-TMAP)P and T (4-HP)P have the highest sensitivity, their molar absorptivity exceeds 10^6. This is rare in spectrophotometry, it can be used to determine ultratrace copper in biological samples. Moreover, its reaction rates are always slow and carried out under heating. In order to speed up the chromogenic reaction, some activators, such as hydroxylamine hydrochloride and ascorbic acid, can improve the rate and have been widely used. On the other hand, the wavelength differences ($\Delta\lambda$) are very small, most of them are almost equal to zero. As copper complex has a high stability in a strongly acidic medium, analysts often increase the $\Delta\lambda$ by adjusting acidity to pH<3. 0 with strong acid after the reaction has been completed. The selectivity of the reaction of copper is often very poor; thus, separation steps were required for determination of trace copper in complex samples.

The reaction of derivatives of porphyrin with zinc are similar to the reaction of copper; Cd (II) and imidazole can often shorten reaction times at room temperature and were selected as activators.

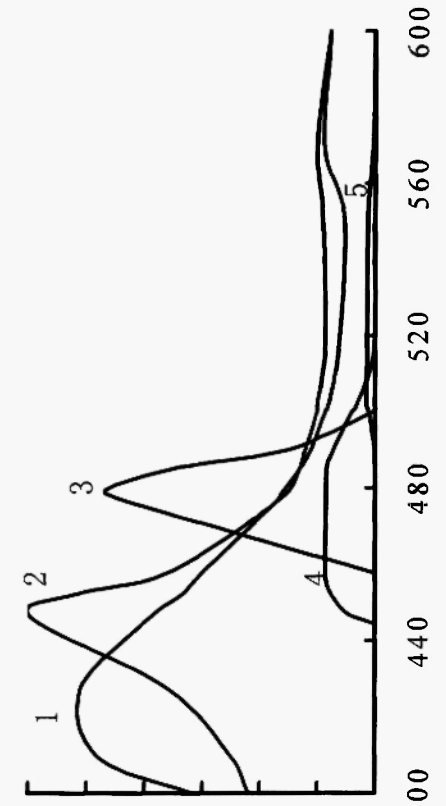


Fig. 7: The effect of different types of surfactants on the reaction of TDBHPP with lead: (1) the absorption spectrum of the reagent in the presence of CTMAB, (2) the absorption spectrum of the reagent in the presence of TritonX-100, (3) the absorption spectrum of the complex in the presence of TritonX-100, 10 μg of lead, (4) the absorption spectrum of the complex in the presence of CTMAB, 10 μg of lead, (5) the absorption spectrum of the complex without surfactant, 10 μg of lead.

Porphyrin has been applied effectively to determination of lead. On the one hand, lead reacts with the reagents sensitively, the complex has good stability and a large $\Delta\lambda$. On the other hand, the reaction is always carried out in an alkaline medium (pH>9. 0), the acidity range is wide and easily controlled. Some excellent reagents with a very good sensitivity and selectivity have been obtained, e.g. T (DBHP)P, and have been used to determine lead in samples; T (DBHP)P has been used to determine trace lead in various complex samples. These methods have an advantage over other lead reagents, such as the derivatives of arsenazo and chlorophosphonazo, as regards sensitivity and stability as well as satisfactory precision and accuracy.

Cadmium reacts with derivatives of porphyrin sensitively; here, T(4-SP)P and T(4-M-3-SP)P are the most sensitive reagents. Unlike other metals, the reaction of cadmium with the reagents can be completed rapidly at room temperature without activators. $\Delta\lambda$ exceeds copper and zinc. The reaction acidity is similar to that of lead (pH>8. 0). As the selectivity was always poor, some separation steps or masking reagents were often used to determine cadmium in real samples.

The reaction of derivatives of porphyrin with palladium is similar to that of copper and zinc. Among the reagents, T (4-HP)P and T (4-DMAP)P have the highest molar absorptivity.

In a weak acid or alkaline medium, manganese (II) can react with derivatives of porphyrin sensitively. The reaction requires heating in the presence of activators, such as ascorbic acid, Cd (II), imidazole, hydrogen peroxide and Pb (II), or without activators.

Porphyrin reagents have also been used for the determination of chromium, bismuth, nickel, cobalt, iron, gold, mercury, rhodium, ruthenium, silver, etc., seventeen metal elements.

The applications of these reagents are listed in Table8.

Table 8

Application of derivatives of porphyrin as chromogenic reagents in analytical chemistry

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
TPP	Cu	SDS	[a]pH=4.7, [b]pH=0.6-1.2	Hydroxylamine hydrochloride	3.0min (100°C)	414	4.76×10^5	/45/
		SDS and CTMAB	[a]pH=4.7, [b]pH=0.6-1.2	Hydroxylamine hydrochloride	15.0min (100°C)	414	4.50×10^5	/46/
	Zn			Acetic acid	60min. (room temperature)	551	0.14×10^5	/47
	Cd	SDS	[a]pH=12.5	Dipyridyl	2.0min (100°C)	432	4.2×10^5	/48/
	Pd	SDS	[a]pH=1.9 [b]pH=1.0			410	1.74×10^5	/49/
$TPPS_3$	Cu		[a]pH=4.0 [b]pH=2.5		1.0min (100°C)	413	4.76×10^5	/50/
	Pb		[a]pH=10.2		5.0 min (70°C)	464	2.75×10^5	/51/

	Cd		[a]pH=12.5	Dipyridyl	4min (room temperature)	432	4.45×10^5	/52/
	Pd		[a]pH=3.0 [a]pH=2.6	[b]Ascorbic acid	7.0min (100°C)	411.6	2.79×10^5	/53/
	Fe		[a]pH=4.0	Ascorbic acid	150min (100°C)	395	1.4×10^5	/54/
T (4-SP)P	Cu		[a]pH=3.5, [b]pH=2.5		1.0min (100°C)	413	3.7×10^5	/55/
		Benzene	[a]pH=4.0, [b]pH=1.0		5.0min (10.J°C)	419	4.6×10^5	/56/
			[a]pH=5.0, [b]1.0 H_2SO_4		4.0min (100°C)		3.7×10^5	/9/
	Fe		[a]pH=4.0		15.0min (100°C)	392	2.07×10^5	/57/
T (4-SP)P	Pb		[a]pH=10.2		5.0min (100°C)	464	2.6×10^5	/58/
			[a]2.0mol.l^{-1} ammonia		1.0min (100°C)		2.6×10^5	/59/
	Zn		[a]Acetic acid (pH=4.5)		4.0min (100°C)	421	4.5×10^5	/60/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
	Cd		[a]pH=8.0		8.0min (room temperature)	432	0.143×10^5	/61/
			[a]2.0mol.l^{-1} ammonia		5.0min (100°C)		4.5×10^5	/59/
			[a]pH=9.0	Imidazole	10.0min (room temperature)	434	4.37×10^5	/62/
			[a]pH=10-12	Dipyridyl	10.0min (room temperature)		4.5×10^5	/63/
	Au	[a]pH=10.2		Cd and diphenyl guanidine	6.0min (100°C)	410	6.65×10^5	/64/
	Bi	SDS	[a]pH=5.9	Cd (II)		466	1.7×10^5	/65/
	Ni		[a]2.0mol.l^{-1} ammonia		30.0min (100°C)		1.66×10^5	/59/
		CTMAB	[a]pH=10.4	Ascorbic acid	32.0min (100°C)	414	2.24×10^5	/66/

	Co		[a]pH=8.5	Imidazole and Cd (II)	Rapid (room temperature)	432	2.44×10^5	/67/
			[a]pH=4.0	Ethylene diamine	7.0 min (100°C)	426	3.54×10^5	/68/
	Hg		[a]pH=6.0		40.0min (room temperature)		5×10^5	/69/
			[a]pH=3.0, [b]pH=1.0		15.0min (100°C)	410	2.2×10^5	/59/
			apH=4.5, bpH=2.5		15.0min (100°C)	412	2.2×10^5	/70/
			[a]pH=4.5, [b]pH=1.5	Ascorbic acid	8.0min (100°C)		2.2×10^5	/71/
	Rh	CTMA		Cd (II)	[a]pH=9	417	5.9×10^5	/12/
	Mn	CTMAB		Ethylene diamine and Cd (II)	2.0min (100°C)	442	3.2×10^5	/72/
		CTMAB	[a]pH=10.4	Ascorbic acid	20min (room temperature)	466	0.67×10^5	/73/
			[a]pH=6.4	Pb (II)	7.0min (100°C)		0.67×10^5	/59/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
T (4CP)P	Cu	SDS	[a] pH=5 5, [b] pH<0. 8	Hydroxylamine	5.0min (100°C)	416	4.2×10^5	/74/
	Zn		[g] pH=9	Dipyridyl	10.0min (room temperature)	433	4.58×10^5	/75/
			[a] pH=7. 5	Cd and imidazole	Immediate	426		/76/
	Mn			Imidazole and Cd (II)	7.0min (100°C)	465	0.979×10^5	/59/
	Cd		[a] pH=9	Dipyridyl	10.0min (room temperature)	433	4.58×10^5	/62/
T (3-MPy)P	Cu	2-nitro-propane	[a] $HClO_4$	Hydroxylamine	1min (room temperature)	419	4.0×10^5	/77/
			[a] pH=5. 0, [b] pH=1. 0	Hydroxylamine and ascorbic acid	7min (room temperature)	419	3.55×10^5	/78/
			[a] pH=6. 0, [b] pH=2. 2		7. 0min (100°C)	420	3.5×10^5	/38/

	Zn		[a]pH=9.3-11.7		5.0min (room temperature)	441	3.61×10^5	/76/
			[b]pH=10.5		2.0min (room temperature)	435	0.186×10^5	/79/
	Cd		pH=9.3-11.7		4.0min (room temperature)	441	3.61×10^5	/80/
	Co		[a]pH=10.2		15.0min (100°C)	432	1.31×10^5	/81/
	Ag		TritonX-100	pH=9.6		5.0min (100°C)	425.5	3.56×10^5	/82/
	Au		0.3mol.l^{-1} H_2SO_4		10.0min (100°C)	402.8	3.24×10^5	/147/
T (4-MPy)P	Cu		[a]pH=9.0, [b]pH=2.0	Cysteine	5.0min (room temperature)	423	3.63×10^5	/83/
			[a]pH=4.5, [b]pH=2.0	Hydroxylamine and ascorbic acid	2.0min (room temperature)	446	2.46×10^5	/78/
	Zn		[a]pH=9.2-10.8		2.0min (room temperature)	437.2	2.28×10^5	/84/
	Cd		[a]pH=8.7-11.1		5.0min (room temperature)	450	2.20×10^5	/80/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
T (4TMAP)P	Cu		[a] pH=4.5, [b] pH<2.8	Hydroxylamine	5.0min (room temperature)	410.5	4.0×10^5	/85, 86/
			[a] pH=4.4	Hydroxylamine	1.0min (100°C)		1×10^7	/87/
			[a] pH=4.5, [b] pH=1.0	Hydroxylamine	5.0min (room temperature)	413	2.5×10^7	/88/
	Fe		[a] pH=4.0, [b] pH=1.0		15.0min (100°C)	395	1.3×10^5	/89/
	Zn		[a] pH=5.0	7-I-8-hydroxyl-quinoline	2.0min (room temperature)	421	5.1×10^5	/90/
			[a] pH=10.2	Hydroxyamine	5.0min (100°C)	425	3.42×10^5	/91/
	Cd		[a] pH=13		2.0min (100°C)	433	5.9×10^5	/59/
			[a] NaOH	8-hydroxyl-quinoline	6.0min (room temperature)	434	4.5×10^5	/92/

	Mn		SLS	Ethylene-diamine and Cd (II)	2.0min (100°C)	437	2.6×10^6	/93/
			[a]pH=9.5		2.0min (100°C)	464	1.13×10^5	/94/
		SDS	[a]pH=10.3	Ethylene-diamine, Cd (II) and Ascorbic acid	1.0min (100°C)			/95/
	Pb	CTMAB	[a]pH=12.3		10min. (room temperature)	462	2.21×10^5	/96/
T (4TMAP)P	Pd		[a]pH=5-6, [b]pH=1.0	Ascorbic acid	2.0min (room temperature)	421	2.5×10^5	/97/
		Trion X-100	[a]pH=3.0, [b]pH=1.0	Ascorbic acid	4.0min (room temperature)		4.9×10^5	/98/
		SDS	[a]pH=3.2,	Ascorbic acid	20.0min (100°C)	436	5.7×10^5	/99/
	Ru	CTMAB	[a]pH=4.0		40mm. (room temperature)	436	5.25×10^5	/100/
	Co		[a]pH=9.5	Ethylene diamine	10.0min (100°C)	427	2.78×10^5	/101/
	Hg	CTMAB	[a]pH=12.3		10.0min (room temperature)	446	2.79×10^5	/96/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
T (5-ST)P	Cu					419.4	2.98×10^5	/102/
	Zn		[a]pH=5-11, [b]pH=3-4		15.0min (100°C)	427.6	4.17×10^5	/102/
	Cd					457.4	3.44×10^5	/102/
	Pd		[a]pH=9.3	Ascorbic acid	20.0min (100°C)	416.6	1.87×10^5	/102/
	Mn				15.0min (100°C)	469	1.32×10^5	/102/
	Co		[a]pH=9.3	8-hydroxyl-quinoline	100°C 10min	432.2	2.27×10^5	/102/
T (4HP)P	Cu	Triton X-100	[a]pH=2.8-3.3	Hydroxylamine	1min (room temperature)	422	3.18×10^6	/102/
	Pb	Triton X-100	[a]pH=10.2		2.0min (100°C)	465	2.59×10^5	/102/

	Zn	Triton X-100	[a]pH=9.9	Activator	2min (room temperature)	446	3.9×10^5	/102/
	Pd	SDS	[a]pH=3.5	Ascorbic acid	15.0min (100°C)	420	1.46×10^6	/103/
		SDS	[a]pH=4.5	Na_2SO_3	10.0min (100°C)		2.3×10^5	/104/
	Cd	Triton X-100	[a]pH=9.1-9.3		Rapid (room temperature)	436	4.72×10^5	/102/
T(4DMAP)P	Pd	Triton X-100 and SDS	[a]pH=3.2		20.0min (100°C)	436	5.6×10^6	/99/
	Cu	SDS and CTMAB	[a]pH=4.7, [b]pH=2.0	Hydroxylamine	15.0min (100°C)	412	3.9×10^5	/105/
		SDS	[a]pH=6.0, [b]0.84 H_2SO_4	Hydroxylamine	5.0min (100°C)	434	3.9×10^6	/106/
$TF_{COOC_2H_5}P$	Cu	SDS and CTMAB	[a]pH=6.0, [b]pH=2.0	Hydroxylamine	15.0min (100°C)	420	1.52×10^5	/107/
m-FTPPS$_4$	Cu		[a]pH=6.0, [b]1.0 H_2SO_4		40min (100°C)		4.4×10^5	/59/
	Pb		[a]2.0mol l^{-1} ammonia		10min (100°C)		2.3×10^5	/59/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
	Zn		[a]pH=4.8, [b]2.8mol.l^{-1} H_2SO_4	Cd^{2+}	8.0min (100°C)		4.36×10^5	/59/
	Pd		[a]pH=4.8, [b]pH=2.5	Ascorbic acid	10min (100°C)	409	1.7×10^5	/59/
m-FTPPS$_4$	Cd		[a]2.0mol l^{-1} ammonia		5.0min (100°C)		4.4×10^5	/59/
m-FTPPS$_4$	Pd		[a]pH=4.5, [b]pH=1.5	Ascorbic acid	80min (100°C)		1.83×10^5	/59/
	Mn		[a]pH=6.4	Pb^{2+}	7.0mim (100°C)		1.2×10^5	/59/
	Ni		[a]2.0mol.l-1 ammonia		30.0min (100°C)		1.8×10^5	/59/
	Co		[a]2.0mol l^{-1} ammonia	Cd (II)	70min (100°C)		3.0×10^5	/59/

	Cd		0.02NaOH		7.0min (100°C)	433	3.32×10^5	/109/
m-ClTPPS$_4$	Cu		[a]pH=6.0, [b]1.0 H_2SO_4		4.0min (100°C)			/59/
	Pb		[a]2.0 mol. l^{-1} ammonia		1.0min (100°C)		1.82×10^5	/59/
	Zn		[a]pH=4.8, [b]2.8mol.l^{-1} H_2SO_4	Cd (II)	8.0min (100°C)		4.18×10^5	/59/
	Cd		[a]2.0mol.l^{-1} ammonia		5.0min (100°C)		4.45×10^5	/59/
	Pd		[a]pH=4.5, [b]pH=1.5	Ascorbic acid	8.0min (100°C)		1.48×10^5	/59/
	Mn		[a]pH=6.4	Pb (II)	7.0min (100°C)		1.28×10^5	/59/
	Ni		[a]2.0mol.l-1 ammonia		30.0min (100°C)		1.61×10^5	/59/
	Co		[a]2.0mol.l^{-1} ammonia	Cd (II)	7.0min (100°C)		3.0×10^5	/59, 110/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Mola- absorptivity	Ref.
m-BrTPPS$_1$	Cu		[a] pH=6.0, [b] 1.0 H_2SO_4		4.0min (100 °C)		2.38×10^5	/59/
			pH=3.0		4.0min (100°C)	412.8	2.61×10^5	/112, 113/
	Pb		[a] 2.0mol l^{-1} ammonia		1.0min (100 °C)		1.44×10^5	/59/
	Zn		[a] pH=4.8, [b] 2.8mol l^{-1} H_2SO_4	Cd (II)	8.0min (100 °C)		4.09×10^5	/59/
			[a] pH=9.5-10	β-cyclodex rin			4.19×10^5	/59, 111/
	Cd		[a] 2.0mol l^{-1} ammonia		8.0min (100 °C)		4.11×10^5	/59/
	Pd		[a] pH=4.5, [b] pH=1.5	Ascorbic acid	5.0min (100 °C)		1.5×10^5	/59/
	Mn		[a] pH=6.4	Pb (II)	8.0min (100 °C)		1.28×10^5	/59/

	Ni		[a]2.0mol. l^{-1} ammonia		30.0min (100°C)		1. 33×10^5	/59/
	Co		[a]2.0mol l^{-1} ammonia	Cd (II)	7.0min (100·C)		2. 73×10^5	/59/
o-C|TPPS$_4$	Cu		[a]pH=5 0, [b]1.0 |H$_2$SO$_4$			4. 02×10^5	/59/
o-C|TPPS$_4$	Pb		[a]2.0mol. l^{-1} ammonia		1.0min (100·C)		2. 4×10^5	/59/
	Zn		[a],H=4 8, [b]2 8mol l^{-1} H,SO$_4$	Cd (II)	1.0min (100·C)			/59/
			[a]2 0mol. l^{-1} ammonia		5 0min (100·C)		5. 1×10^5	/59/
o-C|TPPS$_4$	Pd		[a]pH=4. 5, [b]pH=1. 5	Ascorbic acid	8.0min (100·C)		1. 7×10^5	/59/
	Mn		[a]pH=6. 4	Pb (II)	7.0min (100·C)		1. 27×10^5	/59/
	Ni		[c]2.0mol l^{-1} ammonia		30.0 min (100°C)		2. 09×10^5	/59/
	Co		[a]2 0mol. l^{-1} ammonia	Cd (II)	7. 0min (100°C)		2. 85×10^5	/59/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
o-BrTPPS$_4$	Cu		[a]pH=5.0, [b]pH=1.0 H_2SO_4		40min (100°C)		2.38×10^5	/59/
	Pb		[a]2.0mol.l^{-1} ammonia		10.0min (100°C)		2.05×10^5	/59/
	Cd		[a]2.0mol.l^{-1} ammonia		50min (100°C)		4.34×10^5	/59/
	Pd		[a]pH=4.5, [b]pH=1.5	Ascorbic acid	80min (100°C)		1.23×10^5	/59/
	Mn		[a]pH=6.4	Pb (II)	70min (100°C)		1.15×10^5	/59/
	Ni		[a]2.0mol.l^{-1} ammonia		30.0min (100°C)		1.61×10^5	/59/
	Co		[a]2.0mol.l^{-1} ammonia	Cd (II)	70min (100°C)		2.58×10^5	/59/

T (4-MO-3-SP)P	Cu				4.0min (100°C)	415. 6	3. 18×10^5	/114, 115/
	Zn		[a]pH=5. 2			423. 6	5. 15×10^5	/116/
	Pb		[a] pH=9. 6			464. 8	3. 44×10^5	/114/
			[a] pH=11		15.0min (room temperature)	464. 4	2. 3×10^5	/117/
	Mn			Hydroxylamine and Cd (II)	3.0min (100°C)	469	1. 07×10^5	/118/
	Co		[a]pH=4. 0			426. 8	1. 0×10^5	/114/
	Fe							/119/
T (3-Br-4-H-5-MOP)P	Cu		[a] pH=3-4. 5		4.0min (100°C)	420	2. 4×10^5	/120/
T (3-Br-4-SP)P	Mn	CTMAB	[a]pH=9. 2			444	3. 34×10^5	/74/
	Cu		[a] pH=3. 0		5.0min (100°C)	412. 8	2. 61×10^5	/121/
T (4-MOP)P	Cu	Tween-80	[a]pH=7 05 [b]pH=1. 0		7.0min (100°C)	419	3. 39×10^5	/122/
	Zn	Tween-80	[a]pH=7. 05		15.0min (100°C)	428. 5	4. 95×10^5	/122/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
	Mn	Tween-80	[a]pH=8.8		30.0min (100°C)	430	1.36×10^5	/123/
T (4-M-3-SP)P	Pb		[a] pH=9.6		5.0min (100°C)	464	2.82×10^5	/124/
T (4-M-3-SP)P	Zn		[a]pH=7.8, [b]pH=4.0	Hg (II)	8.0min (100°C)	428	5.2×10^5	/125/
	Cd	CTMAB	[a]pH=10.8	Cd (II)	5.0min (room temperature)	440	7.6×10^5	/126/
T (4-M-3-SP)P	Hg	CTMAB	[a]pH=9.4		5.0min (room temperature)	446	2.45×10^5	/127/
T (4-MAP)P	Pb		[a]pH=10.2		1.0min (100°C)	464	2.8×10^5	/128/
T (4-BrP)P	Cu	Tween-80	[a] pH=9.0		3.0min (100°C)	468	2.87×10^5	/129/

T (2-HP)P	Cu	Triton X-100	[a]pH=9.9-10.7		3.0min (100°C)	467	2.11×10^5	/130/
T (3-HP)P	Cu	Triton X-100	[a]pH=9.3-10.3		3.0min (100°C)	467	2.6×10^5	/130/
	Zn	Triton X-100	[a]pH=10.2 [b]pH=1.0		2.0min (100°C)	425	4.76×10^5	/130/
T (3, 4-DHP)P	Cu	Triton X-100	[a]pH=10-10.7		3.0min (100°C)	472	1.08×10^5	/130/
T (DBHP)P	Pb	Triton X-100	[a] pH>10	8-hydroxyl-quinoline	5.0min (room temperature)	479	2.5×10^5	/131, 132/
	Zn	Triton X-100	[a]pH=10		5.0min (100°C)	447	1.5×10^5	/132/
		Triton X-100	[a]pH=10	Cd and imidazole	5.0min (room temperature)	447	2.6×10^5	/133, 134/
T (4-AOP)P	Zn	SDS	[a]pH=9.9	Cd and imidazole	3.0min (100°C)	435	5.02×10^5	/135/
	Au	SDS and Trition X-100	[a]pH=10-11.2,		6.0min (100°C)	420	1.62×10^6	/136/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
	Ru	Trition X-100	[a]pH=9.7-10.3	Cd (II)	12.0 min (100°C)	421	7.0×10^5	/137/
	Ir	SDS-Triton X-100	[a]pH=9.5-10.5	Cd (II)	15.0 min (100°C)		1.36×0^6	/138/
	Pd	SDS	[a]pH=3.4, [b]0.335mol l^{-1} H_2SO_4		20.0 min (100°C)	416	1.21×10^5	/138/
T (2-H-5-SP)P	Zn		[a]pH=9.9, [b]0.05mol l^{-1} HCl		3.0min (100°C)	420.5	3.59×10^5	/139/
	Mn		[a]pH=9.4	H_2O_2	6.0min (100°C)	413.8	6.4×10^6	/140/
T (4-Cl-3-SP)P	Zn	CTMAB	[a] NaOH		10.0min (100°C)	434.5	1.10×10^5	/141/

T (3-F-4-SP)P	Zn		[a]1.0mol.l^{-1} NaOH		20.0min (100°C)	433	3.32×10^5	/142/
T (4-ClP)P	Pd	SDS	[a]1.0mol.l^{-1} NaOH		Rapid (room temperature)	432	2.46×10^5	/118/
	Co	Triton X 100 +SDS +CTMAB			15.0min (100°C)	420	7.94×10^5	/118/
T (4-ClP)P	Ag	Triton X-100 and CTMAB	[a]NaOH [b]H_2SO_4		9.0min (100°C)	426	3.94×10^5	/126/
T (3-Br-4H-5-MOP)P	Pd		[a]pH=2.5			422	1.3×10^5	/29/
T (2-A-5-SP)P	Co		[a]Ammonia		3.0min (100°C)		1.5×10^5	/143/

Table 8 (continued)

Reagent	Element	Medium	Acidity	Activator	Time of reaction (temperature)	λmax (nm)	Molar absorptivity	Ref.
5, 10, 15-tri (4-sulfono phenyl)-20-/4-/4-/10, 15, 20-tri (4-sulfonophenyl)-5-porphyrin-phenoxy/ proporxy/ phenyl/ porphyrin ($DTPPS_6$)	Cu	Tween-60	[a]pH=3-4. 5		4.0min (100°C)	410	3.52×0^5	/144/
	Cu	Tween-60	[a]H_2SO_1 and H_3PO_4		5.0min (100°C)	440	7.8×10^5	/145/
T (4-H-3SP)P	Ni	Triton X-100	[a]pH=9. 25	Cd (II) and imidazole	6.0min (100°C)		2.23×0^5	/146/

[a]:reaction acidity

[b]:acidity after reaction completed

SDS: sodium dodecyl sulfonate

CTMAB:cetyltrimethyl ammonium. bromide.

OP:p-Octylpolyethyleneglycol phenylether.

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