Trace Determination of Copper(II), Iron(II), Nickel(II), and Zinc(II) Using 3-Phenyl-Rhodanine - An Amperomertric Reagent

Sugam J Shivhare[1*], Rakesh Mishra[2] and Mangla Dave Gautam[3]

[1]*Department of Applied Sciences, SVKM's NMIMS, Mukesh Patel School of Technology Management and Engineering, Shirpur Campus, 425405, India.*
[2]*Department of Applied Sciences, LKCT, Indore, India.*
[3]*Govt. Holkar Science College, Indore, India.*
[*]Corresponding Author

AIM – **Electrochemical studies on heterocyclic compound containing nitrogen is the topic of interest for many researchers. Sulphur containing heterocyclic compounds were used as amperometric reagents. In analytical chemistry rhodanine (2-Sulfanylidene-1, 3-thiazolidin-4-one) and its derivatives are used as amperometric reagents for trace determination of several transition metal ions. In this paper we have synthesized, characterized and has been used 3-phenyl-rhodanine as spectrophotometric reagents for determination of certain metal ions.**

Keywords:- Electrochemical studies, Heterocyclic compounds, Amperometry, Rhodanine, 3-Phenyl Rhodanine

I. INTRODUCTION

In analytical chemistry, rhodanine and its derivatives are highly used as highly sensitive reagents for determination of several metal ions[1,2]. Structurally rhodanine (2-Sulfanylidene-1, 3-thiazolidin-4-one) is a thiazole heterocyclic compound having five member ring with sulfur and nitrogen as hetro center. Carbonyl group on fourth carbon also makes it a wonder molecule. 3-phenyl-rhodanine has been used as a spectrophotometric reagent for determination of ions[3,4]. Due to coordination at the metallic surface, it is an essentially as the mixed-type inhibitor of mild steel in low pH solution[5] and having ability to inhibit the corrosion. Rhodanine and its derivatives was well known spot test reagent and can be used as amperometric reagent. During last few years electrochemical studies on aromatic compounds were subject of many investigations[6,7]. Nowadays electrochemical techniques is well established and widely used in organic chemistry and termed as 'organic polarography'. Amperometric titrations have a wide field of applicability can be accomplished successfully. This is because the readings near the equivalence point have no special significance; hence slight soluble reaction can also be determined. It is highly sensitive technique and used for very dilute solution up to ppm level and usually be carried out rapidly since the end point is found graphically. Its principle was proposed as early as 1897 by Soloman and it was later used by Nerst and Merrian[8]. Heyrovaskey and Berezickey[9] were the first to carry out amperometric titration with indicator electrode DME (dimethyl ether). Kolthoff et al[10,11] exclusively studied theory of such titration. Later estimation of various ions have been done by amperometric titration[12,13]. Amperometric titrations possess greater sensitivity than others suitable electrochemical methods for end-point indication. At low pH by the assembly of polarograph (Systronic Polarograph 1634) with galvanometer titration conducted by using 3-phenyl-rhodanine is used as a reagent in the determination of some ions[14,15]. In present paper we report the synthesis, characterization of 3-phenyl-rhodanine and its application as an amperometric reagent for the determination of some cations.

II. METHODOLOGY

Material and Methods: In organic synthesis it is of immense important to get final product in satisfactory yield along with purity. All the chemical used were of analytical grade reagent. Solvents used during the present work were purified and dried according to standard method. The synthesized compound was analyzed with Infrared red spectra, ^{1}H NMR, Mass spectral. Purity of synthesized compounds was checked by TLC on silica gel. Melting points was taken in open capillary tubes using electric melting point apparatus and are uncorrected.

Preparation of 3-Phenyl rhodanine

Aniline (21.7g) was dissolved in a mixture of ethanol (30 ml) and diethyl ether (20 ml) in a 250 ml Erlenmeyer flask. Carbon disulphide (22 ml) was cooled in an ice bath and added slowly in above mixture; carbon tetra chloride (20 ml) was added. In a beaker Sodium Chloroacetate (25.6g) was dissolved in water (60ml) and neutralized with anhydrous sodium carbonate. This solution was heated to $35^{\circ}C$ and maintained this temperature, while the dithiocarbamate was added with continuous stirring. The resulting solution was poured slowly into hot 80ml of 6n hydrochloric acid, which was heated to $90\text{-}95^{\circ}C$ for further 15 minutes. The white

suspension produced was neutralized with strong ammonia. The yellow oil that solidify on cooling; further crystallization also occurred. All solids were filtered off and washed well with water. More ammonia was added to the combined filtrate and wash until no more precipitate was obtained. The 3-phenylrhodanine (fig.1.) separates as pale yellow crystals. They were recrystallized from alcohol or acetone. Yield = 16g (74%); Melting point 189°C;

Detection Method

Structure of the synthesized rhodanine and its derivatives have been characterized on the basis of their IR, ^{1}H-NMR and Mass spectral studies. An overview of structure determination via various spectroscopic methods is as following:-

IR Spectral Studies: The presence of C=O stretching absorption band in the region 1745-1710 cm^{-1} instead of 1750-1740 cm^{-1} is due to the partial enolisation of carbonyl group attached to methylene group in rhodanine it appear at 1739 cm^{-1} and in 3-phenyl-rhodanine it appears at 1742 cm^{-1} Furthermore the presence of double bond in conjugation with C=O group lowers the frequency to 1690-1675 cm^{-1} is due to the partial enolisation of carbonyl group appear at 1680 cm^{-1}. When methylene group is adjacent to carbonyl and Sulphur group; it exhibits characteristic peaks in the region 2960-2940 cm^{-1} and 1450-1428 cm^{-1}.

The substitution pattern of ring appear in the region 605-415 cm^{-1} Furthermore, a few characteristic peak at 1210-1040 cm^{-1}, 1110-1015 cm^{-1} and 705-605 cm^{-1} are due to the C=S/S-C=S/C-N and C-S-C/C-S vibrational mode respectively when C-S conjugated with double bond a low frequency shift appear in the region 508 cm^{-1}.

^{1}HNMR Spectral Studies: ^{1}HNMR Spectral Studies of 3-phenyl-rhodanine shows doublet at 4.34 and 4.79, since methylene moiety is chemically equivalent but magnetically non-equivalent[8]. The broad hump of multiple in the region 7.26 – 7.50 is assignable to substituted aromatic ring proton[9].

Mass Spectral Studies: 3-phenyl-rhodanine shows the base peak at m/z=150 due to stability of the molecule. Other ion peaks at m/z=89, 107,120,136,165,195 the M[+1] peak is observed at 210 supports the predicted structure of 3-phenyl-rhodanine compound (tab. 1)

Electrochemical Behaviour of 3-phenyl rhodanine

Electrochemical behavior of 3-phenyl-rhodanine has been investigated by a typical experiment with $2.0*10^{-5}$M solution of the compound. The solution was prepared by mixing appropriate quantity of stock solution with 30% v/v dimethylformamide – B.R. Buffer, 30 ml of 0.1M potassium chloride solution, 0.5 ml of fresh solution of gelatin 0.001% w/v and 10ml 30% v/v dimethylformamide (DMF) – Briton Robinson buffer at pH 6.75. Polarogram were recorded after removal of oxygen by passing a stream of purified nitrogen gas for fifteen minutes. A well-defined cathodic wave was

obtained.

The polarogram were recorded after deaeration with purified nitrogen gas for 15-20 minutes and was noticed that half wave potential were shifted towards more negative potential with increase in concentration of depolarizer. It indicated the irreversible nature of electrode process.

The dependence of wave height and half wave potential on pH was investigated by recording the polarogram of $1.0*10^{-5}$M concentration of 3-Phenylrhodanie in 30% v/v dimethylformamide – B.R. Buffer at varying pH 4 to 11. Protons participate in reduction which is observed by linear relationship between half wave potential and pH.

It was observed that with increase in composition of solvent the half wave potential $E_{1/2}$ shifted towards the more negative potential with decreasing the diffusion current (id μA) value. Well-defined polarographic wave was observed at high percentage of solvent (Table.-2-5).

III. FIGURES AND TABLES

Fig. 1

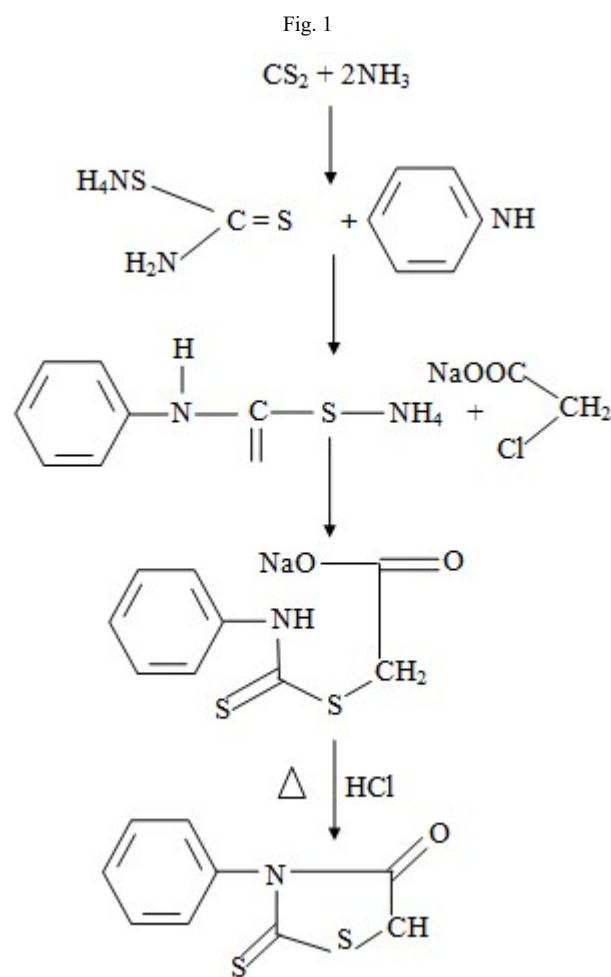Scheme 1: An overview of synthesis of 3- phenyl rhodanine

Fig. 2 Concentration of 3-Phrh 0.050mM / 10ml; Concentration of Cu(II) : 0.050mM/ml
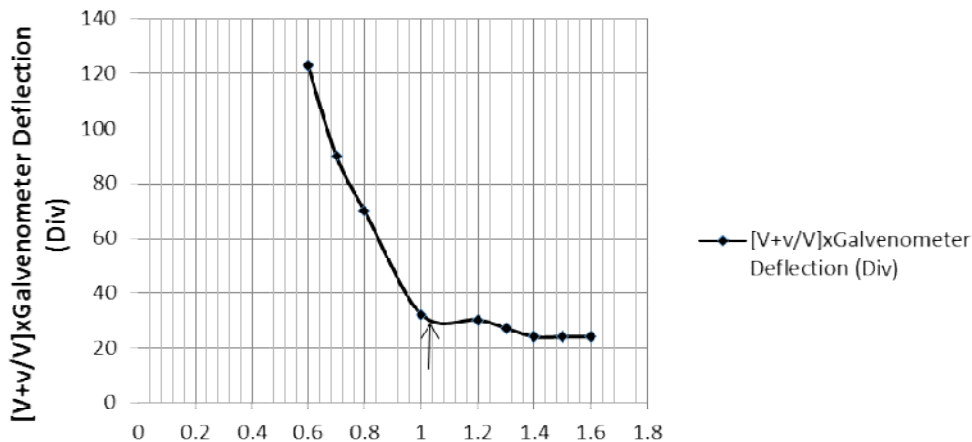

Fig. 3 Concentration of 3-Phrh: 0.050mM / 10ml; Concentration of Fe(II) : 0.050mM/ml

Standard deviation: ± 0.17   Coefficient of variation: 1.0
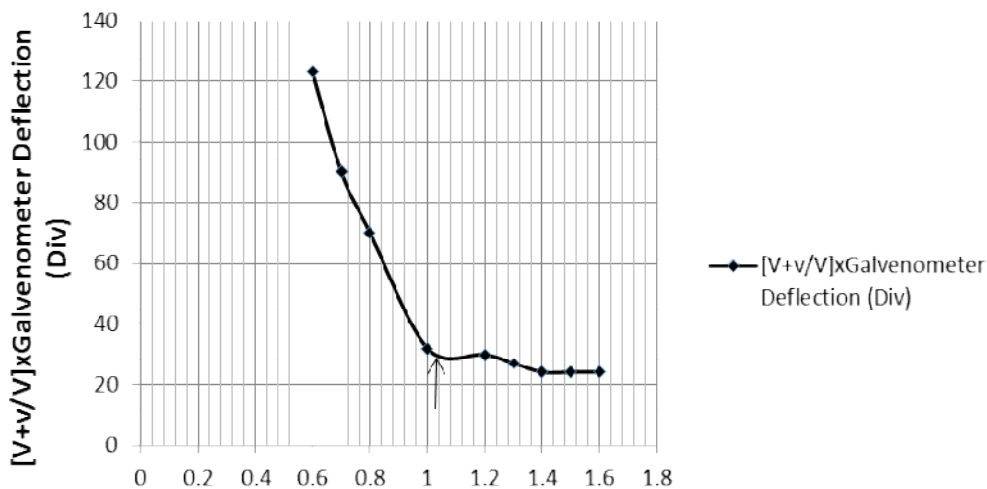

FIG. 4 CONCENTRATION OF 3-PHRH: 0.050MM / 10ML CONCENTRATION OF NI(II) : 0.050MM/ML

Standard deviation: ± 0.45   Coefficient of variation: 1.00
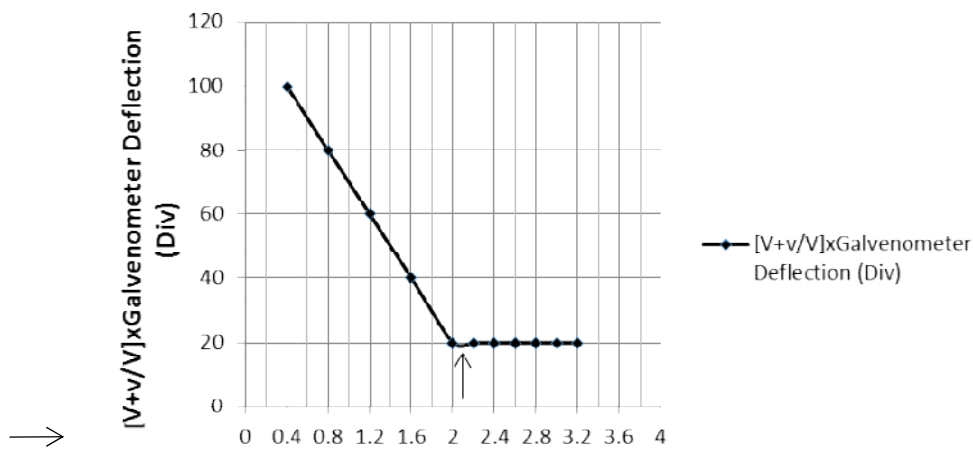
Fig. 5 Concentration of 3-Phrh: 0.050mM / 10ml Concentration of Zn(II) : 0.050mM/ml

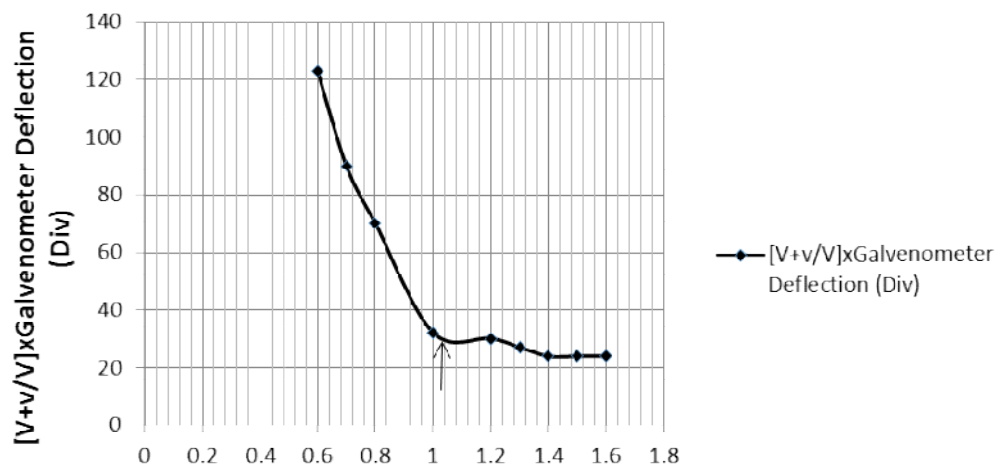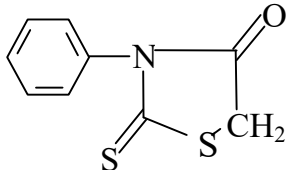Standard deviation: ± 0.49   Coefficient of variation: 0.97

TABLE 1: PHYSICAL CHARACTERIZATION

No.	Structure	M.P. (^{0}c)	Yield (%)	Molecular Formula	Elemental analysis (%)			
					C	H	N	S
1.		189	74%	$C_9H_7NOS_2$	52.05 (51.65)	3.18 (3.38)	6.82 (6.70)	29.98 (30.65)
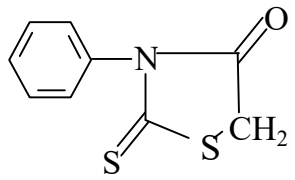
Compounds	IR(v,cm^{-1})	^{1}NMR (**Error! Reference source not found.** ppm)	Mass (m/z,%RA)
	3056, (-CH str.) 2969 ($_v$CH$_2$) and 1455 (**Error! Reference source not found.**CH$_2$) 1590 1495, (C=C aromatic ring str.), 1736 (C=O), 1241, 1347, 1386, (CN), 1170 (C=S), 1053 (S-C=S) 824,834 (out of plane –CH bending vib), 756, 784 (Sub. Phenyl ring str.0 658,692(C-S)	4.33 (d,1H$_1$CH$_2$), 1.76 (d,1H$_1$CH$_2$), 7324-7.55 (m, 5H$_1$ C$_6$H$_5$)	209 [m+,22], m/z = 154 [M+,100], 210 [M^{+1}, 70]

TABLE 2: VALUE OF HALF WAVE POTENTIAL –E$_{1/2}$ V AND DIFFUSION CURRENT IF µA INITIAL VOLTAGE = ZERO, CURRENT RANGE = 20µA, PH =. 10±0.1

S. No.	Approx. Concentration	Amount of Copper (II) (mg)		Percentage Error (%)
		Taken	Found	
1.	3.0×10^{-5}	0.1906	0.1892	-0.73
2.	4.3×10^{-5}	0.2732	0.2745	0.48
3.	5.5×10^{-5}	0.3495	0.3506	0.31
4.	6.3×10^{-5}	0.4003	0.4011	0.20
5.	7.3×10^{-5}	0.4638	0.4631	-0.15
6.	9.0×10^{-5}	0.5719	0.5726	0.12
7.	1.1×10^{-4}	0.6989	0.6999	0.14

TABLE 3:
VALUE OF HALF WAVE POTENTIAL –E1/2 V AND DIFFUSION CURRENT IF µA INITIAL VOLTAGE = ZERO,
CURRENT RANGE = 20µA, PH =. 10±0.1

S. No.	Approx. Concentration	Amount of Iron (II) (mg)		Percentage Error (%)
		Taken	Found	
1.	2.50×10^{-5}	0.1396	0.1374	-1.58
2.	4.50×10^{-5}	0.2512	0.2522	0.40
3.	6.50×10^{-5}	0.3628	0.3634	0.17
4.	9.30×10^{-5}	0.5191	0.5193	0.04
5.	1.30×10^{-4}	0.7257	0.7263	0.08
6.	1.50×10^{-4}	0.8373	0.8377	0.05
7.	2.10×10^{-4}	1.1723	1.1728	0.04

TABLE 4:
VALUE OF HALF WAVE POTENTIAL –E1/2 V AND DIFFUSION CURRENT IF µA INITIAL VOLTAGE = ZERO,
CURRENT RANGE = 20µA, PH =. 10±0.1

S. No.	Approx. Concentration	Amount of Nickle (II) (mg)		Presentage Error (%)
		Taken	Found	
1.	2.20×10^{-5}	0.1290	0.1272	-1.40
2.	4.20×10^{-5}	0.2464	0.2452	-0.49
3.	6.50×10^{-5}	0.3813	0.3821	0.21
4.	7.20×10^{-5}	0.4399	0.4411	0.27
5.	9.002×10^{-5}	0.5279	0.5288	0.17
6.	1.30×10^{-4}	0.7625	0.7631	0.08
7.	2.00×10^{-4}	1.4664	1.4666	0.01

TABLE 5
VALUE OF HALF WAVE POTENTIAL –E1/2 V AND DIFFUSION CURRENT IF µA INITIAL VOLTAGE = ZERO,
CURRENT RANGE = 20µA, PH =. 10±0.1

S. No.	Approx. Concentration	Amount of Zinc(II) (mg)		Percentage Error (%)
		Taken	Found	
1.	3.20×10^{-5}	0.2092	0.2068	-1.15
2.	4.50×10^{-5}	0.2942	0.2925	-0.58
3.	5.50×10^{-5}	0.3596	0.3602	0.17
4.	7.30×10^{-5}	0.4773	0.4785	0.19
5.	9.20×10^{-5}	0.6015	0.6019	0.07
6.	1.30×10^{-4}	0.8499	0.8502	0.06
7.	2.00×10^{-4}	1.6344	1.6348	0.02

IV. RESULT

3-phenyl-rhodanine is polarographically active and gives a well-defined cathodic wave. The wave is irreversible and value of $E_{1/2}$ shift to more negative potential with increase in concentration of depolarizer. By using fresh solution 3-phenyl-rhodanine (B.R. Buffer – 30% v/v dimethylformamide) which is used as titrant, titration was performed by passing nitrogen gas experimental set before addition of titrant from micro burette. The current was noted with galvanometer. L-shaped curves were observed by plotting [(V+v/v)] x I against volume of titrant (Fig. 1-4). End point is located at the intersection of two straight lines which indicated metal to ligand ratio.

Copper	:	3-Phrh	1	:	1
Iron	:	3-Phrh	1	:	2

| Nickel | : | 3-Phrh | 1 | : | 2 |
| Zinc | : | 3-Phrh | 1 | : | 1 |

It is observed that the ultra-micro quantity of Cu(II), Fe(II), Ni(II) and Zn(II) have been determined by the proposed procedure using the 3-phenyl rhodanine. The amount of metal ions was detected with less than ± 1% practical error, with minimum detection limit of 0.25mg approx.

The precision of the procedure was checked up by carrying replicate determinations. The standard deviation was found for Cu(II) 0.17, Fe(II) 0.36, Ni(II) 0.45 and for Zn(II) 0.49 which was less than 1% and coefficient of variation is in between 0.9 to 1.0%.

V. CONCLUSION

Thus, it could be concluded from the data, that the synthesized compound is sensitive, useful and selective amperometric regent for metal determination with ± 1% practical error, minimum detection limit of 0.20 mg approx.

ACKNOWLEDGMENTS

REFERENCES

[1]. Varsha Kshirsagar, Mangla Dave Gautam, Rasayan Journal of chemistry, **2010**, 3,772-776.
[2]. J.H. Yoe and L.G.J. Overholser, *Amer. Chem Soc.* **1941**, *63*, 3224.
[3]. K.Y.Chiu, T.H. Su, C.W.Huang, G.S. Liou and S.H.J.Cheng, Electroanalysis.**2005**, *578*, 283.
[4]. M.C.Corredor and J.M.R.Mellado, Electrochimica Acta.**2004**, *49*, 1843.
[5]. L.D. Hicks, A.J.Fry, and V.C. Kurzweil, Electrochimica Acta. **2004**,*50*,1039.
[6]. Y.I. Moharram and M.M.Ghoneim, J. Electroanal. Chem. **2004**, *35*, 570.
[7]. G. Diao and W. Zhou, J. Electroanal.Chem. **2004**, *32*,567.
[8]. W. Nerst and E.S.Merriam, Physik Chem.**1995**, *53*, 235.
[9]. S. Berezickey and J. Heyrovaskey, Collection Czech. Chem. Commun. **1929**,*1*,19.
[10]. N.V. Rees, J.D. Wadhawan, O.V.Klymenko, B.A. Coles and R.G. Compton, J. Electroanal.Chem. **2004**,*563*,191.
[11]. Sugam Shivhare, Rakesh Mishra, Anil Gharia, and Mangla Dave Gautam, International Journal of Pharmacy and Pharmaceutical Sciences. **2012**, *4*, 374-377.
[12]. N. Laventis, G.Zhang, A.M.Rawashdeh, and C.M.Lenventis, Electro-Chimica Acta. **2003**, *48*, 2799.
[13]. M.J. Higuera, M.R.Montoya, M.R.Galvin, and J.M.R. Mellado, J. Electro- anal. Chem. **2004**,*474*,174.
[14]. L.J.Smith, I.M.Kolthoff and L.J.J.Spillane, Am Chem. Soc.**1942**, *64*, 646.
[15]. S. Bollo, L.J.Nunez-Vergara and J.A.Squella, Bull. Soc. Chill. Quim. **1999**, *44*, 67.