INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Liquid Liquid Extraction and Simultaneous Spectrophotometric Determination of Nickel and Cobalt by PAR with Orthogonal Signal Correction-Partial Least Squares

Reza Moradi[1]

[1]Young Researchers Club and Elites, Toyserkan Branch, Islamic Azad University, Toyserkan, Iran

Abstract—Partial least squares modeling is a powerful multivariate statistical tool applied to extraction spectrophotometric simultaneous determination of mixtures of nickel and cobalt. The method is based on the formation of complexes of 4-(2-pyridylazo) resorcinol (PAR) with nickel and cobalt. The PAR complexes are quantitatively extracted into dichloromethane and the resolution of the mixtures is accomplished by partial least squares (PLS). Orthogonal signal correction (OSC) is a preprocessing technique used in the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for partial least squares calibration of mixtures without loss of prediction capacity using spectrophotometric method. In this study, the calibration model is based on absorption spectra in the 350-750 nm range for 25 different mixtures of nickel and cobalt. Calibration matrices ranges were 1.0-300.0 and 1.0-200 ng ml^{-1} for nickel and cobalt, respectively. A series of synthetic solutions containing different concentrations of nickel and cobalt was used to check the prediction ability of the PLS and OSC-PLS models. The RMSEP for nickel and cobalt with OSC and without OSC was 0.243 and 0.339, 0.502 and 0.622, respectively. The method was successfully applied to the analysis of spiked water (river, tap and well) samples.
Keywords—Nickel, Cobalt, PAR, OSC-PLS, Liquid- liquid extraction

I. INTRODUCTION

Over the past decade the use of simultaneous analysis of multi-component systems with absorption spectroscopic methods has increased strongly. Liquid- liquid extraction methods for the separation and determination of nickel and cobalt are limited [1]. Many of the systems employ on-line separation of the analyte from specific interferences. 4-(2-pyridylazo) resorcinol (PAR) [2] is an excellent complexometric indicator and potentiometric reagent for determination of many metal ions. PAR is a classical example (but not the only one) of a pH dependent non-specific, non-selective color reagent. Partial least squares (PLS) are the widely used regression method in chemometrics [3-4]. On the contrary to what occurs with principal component regression (PCR) calibration for a PLS calibration it is known that information from the concentration values is introduced into the calculation of the so-called latent variables; thus, it is may be that the eliminating wavelengths after variable selection, change the structure and/or the order of the latent variables of the PLS model. The basic concept of PLS regression was originally developed by Wold [5-6] and application of PLS in spectrophotometric data have been discussed in several studies [7-12]. Orthogonal signal correction (OSC) [13] was introduced by Wold et al. to remove systematic variation from the response matrix (absorption) that is unrelated, or orthogonal, to the property matrix (concentration). Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups have published various OSC algorithms [14-16] in an attempt to reduce model complexity by removing orthogonal compounds from the signal. Recently, application of orthogonal signal correction in spectrophotometry for simultaneous determination by PLS has been reported [17]. In this study, extraction and measurement of nickel and cobalt complexes formed by two cations with the reagent 4-(2-pyridylazo) resorcinol (PAR) has been done.

II. EXPERIMENTAL

A. Instrumentation and software

Spectrophotometer (Agilent) HP8453 equipped with a quartz cell pathlength of 1 cm and Chemstation program (Agilent Technology) were used to measure the absorption spectrum. pH meter device Horiba (M-12) was used to adjust pH which it had been calibrated with two standard buffers (pH 4 and 9). Microliter syringe (Hamiltonian) was used to inject small amounts of metals. Data was processed by MATLAB software (ver-6.5) and the PLS-Toolbox (ver-2).

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

B. Reagents

Nitrate salts of nickel, cobalt nitrate, reagent 4-(2-pyridylazo) resorcinol, acetic acid, boric acid and phosphoric acid of with analytical grade were prepared from Merck Company. Distilled water (distilled twice) was used to produce the solution. Stock solutions of 1000 µg ml^{-1} solution contain nickel (II) and cobalt (II) was prepared by dissolving the appropriate amount of the respective salts in distilled water. Also stocks solution of 4-(2-pyridylazo) resorcinol with concentration of 1.17×10^{-3} M was produced by dissolving the appropriate amount of reagent in acetone and ethanol solvents.To adjust the pH the universal buffer, that is, the mixture of mentioned three acid (acetic acid, phosphoric acid, boric acid) was used and to adjust the required pH, sodium hydroxide and hydrochloric acid were used as well.

C. Procedure

Determination of the optimal, in a 50 mL volumetric flask, 0.2 mL 4-(2-pyridylazo) resorcinol, 2mL buffer pH=10 was poured and then distilled twice with distilled water was brought to volume. The metal injection was done with syringe Hamiltonian. In the next stage solutions were transferred to a separator funnel that 4mL of extraction solvent dichloromethane was added to the solution. After that solutions were shaken in the separator funnel for 5 minutes, and it was allowed that two phases became completely separated. When the organic phase, containing the above ligand, is contacted with aqueous phase containing nickel (II) and cobalt (II), complex formation is occurred between ligand with nickel (II) and cobalt (II) and they are brought to the organic phase simultaneously. Quantitative measurements have been done based on absorption read in the organic phase. Spectrum in the wavelength range 350-750 nm will be reviewed.

III.RESULTS AND DISCUSSION

A. Spectral Studies

Measurement in this study is based on nickel and cobalt complexes formed with the cations reagent 4-(2-pyridylazo) resorcinol. The absorption spectrum of reagent, nickel and cobalt complexes at pH=10 is shown in the Fig. (1). As can be observed absorption spectra have a lot of overlapping and asimultaneous measurement of the two cations can't be done by classical methods. The most important advantage of the multivariate calibration methods is that it can be determined one or more component concentrations in the presence of other species simultaneously in a complex matrix.
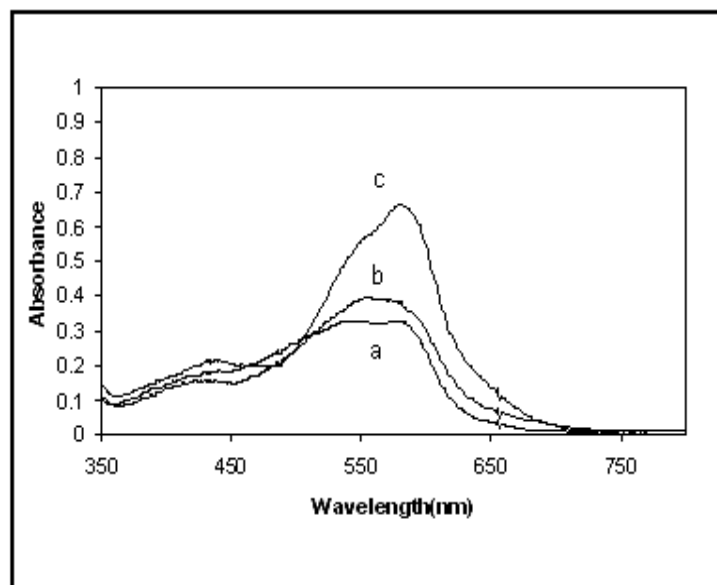

Fig. 1 Absorption spectra of: (a) 4-(2-pyridylazo) resorcinol (9.4×10^{-5} M), (b) 150 PPb Cobalt, (c) 150 PPb Nickel

B. The concentration of reagent 4-(2-pyridylazo) resorcinol

In this study, selecting the concentration is one of the main and very important factors. This amount must be to the point that we can say surely that there is sufficient amount or even more than required amount to form desired metal complex with the ligand. In this study, the reagent concentrations 9.4×10^{-5} M is selected.

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

C. Selection the optimum pH

pH can be cited as another factor affecting the formation of complex. To obtain optimum pH should be noted that in this pH the lowest overlap and the highest absorption exists. In this study, to do this selected pH range between 1-12 for reaction with the fixed metal concentrations media was recorded spectra of both nickel and cobalt metals separately and the best pH had selected. pH=10 as to determine the optimum pH was chosen because the linear region in the pH minimum overlap and maximum absorption of the complexes. Fig. (2) is shown the effect of pH changes.
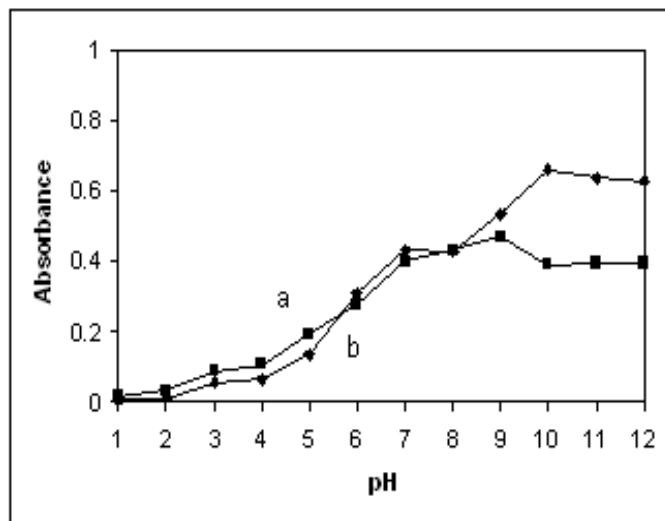

Fig. 2 Effect of pH changes on the formation of complexes (a) Nickel, (b) Cobalt

D. The volume of extraction solvent

In this study, dichloromethane (CH_2Cl_2) was used as the extraction solvent. To evaluate the efficiency of extraction, volume of solvent consumption, as follows accomplished that the different volumes of solvent were added to the solution. Then absorption intensity of extracted organic phase was measured. Fig. (3) Show clearly that there are excellent logical relationships between the intensity of absorption and solvent volume consumed, so that, as the volume of solvent increases, absorption intensity decreases. This fact shows that increasing the volume of solvent 5 to 7 mL, has no positive effect on the extraction amount and just causes dilution and loss of organic phase absorption. So it can be concluded that the optimal amount of solvent consumption volume is 4 mL.
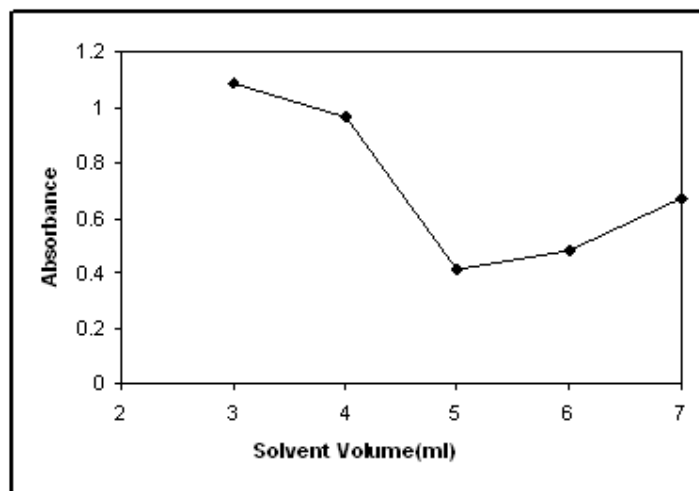

Fig. 3 Effect of volume changes of solvent consumption on absorption intensity of complexes

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

E. Univariate linear calibration

One variable calibration curve plotted based on absorption by the standard sample concentration, under optimal conditions obtained in previous stages, the plotted calibration curves can see in Fig. (4). Wavelengths selected for drawing calibration curves for nickel and cobalt is 580 and 558 nm, respectively. Also the calibration equation and correlation coefficient is shown in figures that linear range regard with the obtained results for nickel is 1-300 ng mL^{-1} and for cobalt is 1-200 ng mL^{-1}, which equations is equivalent to the following.
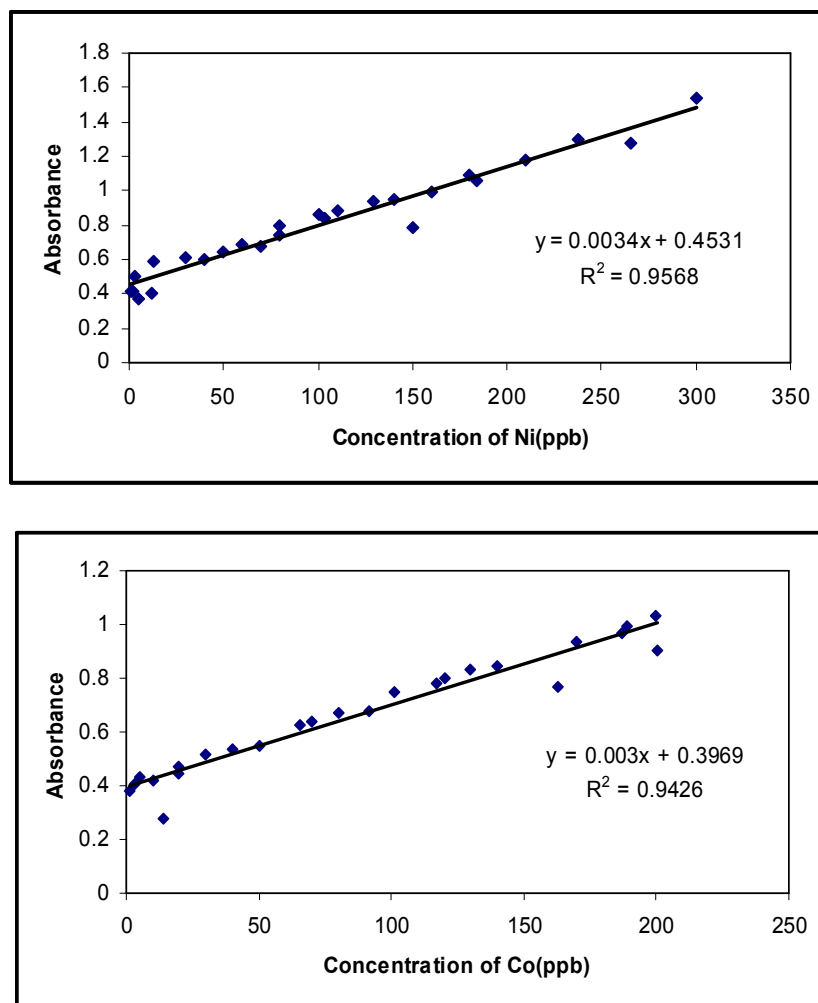

Fig. 4 One variable linear calibration curves of Nickel and Cobalt

F. Multivariate calibration

It is impossible to measure simultaneously the mixture of nickel and cobalt by spectrophotometry because of spectral overlap by classical methods. That's why this problem will be fixed by multivariate calibration. As in the Introduction section explains the multivariate calibration methods like partial least squares (PLS) are composed from two steps; calibration (training) and test (prediction). To get the best results in the calibration stage, we have developed 25 mixtures (Table 1) that the species concentration changes measured in the linear range of species. Then assessment of designed calibration model is made of synthetic samples (Table 2). Absorption of Mixtures in the wavelength 350-750 nm under optimal conditions will be recorded according to methods described. This information would be used for analysis of models using PLS and OSC-PLS.

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Table I

Concentration data of the different mixtures used in the calibration set for the determination of Nickel and Cobalt (ng mL^{-1})

Mixture	Co^{2+}	Ni^{2+}	Mixture	Co^{2+}	Ni^{2+}	Mixture	Co^{2+}	Ni^{2+}
M1	1	1	M10	50	300	M19	150	225
M2	1	75	M11	100	1	M20	150	300
M3	1	150	M12	100	75	M21	200	1
M4	1	225	M13	100	150	M22	200	75
M5	1	300	M14	100	225	M23	200	150
M6	50	1	M15	100	300	M24	200	225
M7	50	75	M16	150	1	M25	200	300
M8	50	150	M17	150	75			
M9	50	225	M18	150	150			

Table II

Added concentrations and measured Nickel and Cobalt in synthetic samples (ng mL^{-1})

Added		Found (PLS)		Error (%)		Found (OSC-PLS)		Error (%)	
Cobalt	Nickel	Cobalt	Nickel	Cobalt	Nickel	Cobalt	Nickel	Cobalt	Nickel
2.0	2.0	2.10	1.90	1.10	-6.00	2.01	1.99	0.50	-7.89
2.0	250.0	1.93	263.21	-5.00	5.62	1.98	251.10	-7.30	0.44
70.0	90.0	72.30	85.14	2.70	-7.22	70.05	90.01	0.05	0.01
70.0	280.0	73.12	271.10	3.50	-6.66	70.10	279.20	1.00	-8.38
120.0	170.0	126.18	161.88	5.30	-4.10	120.15	169.18	1.40	-6.87
160.0	2.0	151.50	1.68	-3.00	-2.99	159.68	1.99	-6.00	-7.89
160.0	250.0	153.10	259.25	-4.19	2.43	159.71	251.08	-6.10	0.43
180.0	90.0	186.71	84.21	4.70	-7.00	180.12	91.03	0.06	1.14
180.0	250.0	183.23	241.30	2.35	-5.23	180.33	249.26	0.18	-6.63
180.0	280.0	173.09	292.10	-2.80	6.30	180.10	279.76	0.05	-8.99
NF [a]		5	4			2	2		
PRESS		0.280	0.342			0.006	0.004		
RMSEP		0.622	0.502			0.339	0.243		
RSEP (%)		5. 008	4. 928			2.555	2.439		
γ [b]		95	99			80	87		
LOD [b]		0.33	0.39			0.22	0.27		

[a] Number of factor.

[b] γ (analytical sensitivity) = SEN/[V(R)]$^{1/2}$ where SEN is the sensitivity (estimated as the net analyte signal) and V(R) is the variance of the instrumental signal and LOD (limit of detection) = 3.3s(0) where s(0) is the S.D. in the predicted concentration of Nickel and Cobalt in a blank sample.

G. Simultaneous measurement of nickel and cobalt in real samples

Proposed method for the simultaneous spectrophotometric measurement of nickel and cobalt was applied successfully in the real samples. Used real samples in this method are water samples (river water, tap water and well). To check ability of the proposed method for measuring nickel and cobalt in the real samples the study of recovery value is used. Table 3 shows the results obtained for real matrix samples. The precision of the method was investigated by the analysis of the samples in the real samples three times each. The result showed that the relative standard deviation (R.S.D.) obtained was acceptable (Table 3). Therefore, the OSC -PLS model is able to predict the concentrations of nickel and cobalt in real matrix sample.

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Table III

OSC -PLS results applied on the real samples (ng mL^{-1})

Samples	Ni^{2+}				Co^{2+}			
	Added	Determined[a]	S.D.[b]	Recovery(%)	Added	Determined[a]	S.D.[b]	Recovery (%)
River water	-	0.19	0.12	-	-	< 0.04	-	-
	0.17	0.35	0.10	90.0	0.22	0.21	0.11	-
Tap water	-	0.25	0.14	-	-	< 0.03	-	-
	0.35	0.62	0.11	92.0	0.19	0.20	0.10	-
Well water	-	0.22	0.14	-	-	0.11	0.10	-
	0.11	0.40	0.13	98.0	0.17	0.28	0.06	95.0

[a] Average of three separate determination.

[b] Standard deviation for n = 3.

IV.CONCLUSIONS

A new method for simultaneous measurement of nickel and cobalt is presented by using UV-vis spectrophotometer and using partial least squares (PLS) and orthogonal signal correction (OSC) preprocessing. Based on absorption spectra and because of excessive overlap, such simultaneous measurement of nickel and cobalt is not possible by classical methods. A simple, sensitive, inexpensive and uncontaminated method to measure nickel and cobalt simultaneously is presented in which all affecting parameters are studied and optimized. According to the results presented, this method has a low detection limit and appropriate standard deviation values and finally this method to measure the nickel and cobalt in synthetic samples was used.

V. ACKNOWLEDGMENT

REFERENCES

[1] R.E. Kitson, Simultaneous spectrophotometric determination cobalt, copper, and iron, Analytical Chemistry., vol. 22, pp. 664-667, 1950.

[2] A. Niazi, A. Yazdanipour, Simultaneous spectrophotometric determination of cobalt, copper and nickel using 1-(2 thiazolylazo)-2- naphthol by chemometrics methods, Chin. Chem. Lett., vol. 19, pp. 860-864, 2008.

[3] J.M. Chilton, Simultaneous colorimetric determination of copper, cobalt, and nickel as diethyl dithio carbamates, Analytical Chemistry., vol. 25, pp. 1274-1275, 1953.

[4] E. Lundberg, Simultaneous determination of manganese, cobalt, and copper with a computer-controlled flameless atomic absorption spectrophotometer, Analytical Chemistry., vol. 48, pp. 1907-1910, 1976.

[5] J. Mi, Y. Li, X. Zhou, B. Zheng, Y. Zhou, Simultaneous determination of iron, copper and cobalt in food samples by CCD-diode array detection-flow injection analysis with partial least squares calibration model, Journal of Physics., vol. 28, pp. 66-69, 2006.

[6] H. Eskandari, A.G. Saghseloo, M.A. Chamjangali, First- and second-derivative spectrophotometry for simultaneou determination of copper and cobalt by 1-(2-Pyridylazo)-2-naphthol in Tween 80 micellar solutions, Turkish Journal of Chemistry., vol. 30, pp. 49-63, 2006.

[7] J. Ghasemi, A. Niazi, A. Safavi, Simultaneous catalytic determination of cobalt, nickel, and copper using resazurine sulfide reaction and partial least squares calibration method, Analytical Letters., vol. 34, pp. 1389-1399, 2001.

[8] J. Ghasemi, Sh. Ahmadi, K. Torkestani, Simultaneous determination of copper, nickel, cobalt and zinc using zinconas a metallochromic indicator with partial least squares, Analytica Chimica Acta., vol. 487, pp.181-188, 2003.

[9] J. Ghasemi, N. Shahabadi, H.R. Seraji, Spectrophotometric simultaneous determination of cobalt, copper and nickel using nitroso-R-salt in alloys by partial least squares, Analytica Chimica Acta., vol. 510, pp. 121-126, 2004.

[10] B.S. Rao, K. Ramakrishna, P. Venkateswaralu, New simultaneous method for the determination of cobalt (II) and copper (II) by atomic absorption spectrometry in industrial effluents and some fruits, Indian Journal of Environmental Protection., vol. 23, pp. 1141-1145, 2003.

[11] M. Ghaedi, E. Asadpour, A. Vafaie, Simultaneous preconcentration and determination of copper, nickel, cobalt, lead, and iron content using a surfactant-coated alumina, Bulletin of the Chem. Society of Japan., vol. 79, pp. 432- 436, 2006.

[12] M.B. Gholivand, Y. Mozaffari, Sh. Sobhani, J. Ghasemi, Simultaneous spectrophotometric determination of trace amounts of cobalt, nickel, and copper using the partial least-squares method after the preconcentration of their 2-aminocyclopentene-1-dithiocarboxylate complexes on microcrystalline naphthalene, Journal of Analytical Chemistry., vol. 63, pp. 232-238, 2008.

[13] Z.T. Jiang, J.C. Yu, H.Y. Liu, Simultaneous determination of cobalt, copper and zinc by energy dispersive X-ray fluorescence spectrometry after preconcentration on PAR-loaded ion-exchange resin, Analytical Sciences., vol. 21, pp. 851-854, 2005.

[14] C. Lu, J.M. Lin, C.W. Huie, M. Yamada, Simultaneous determination of copper(II) and cobalt(II) by ion chromatography coupled with chemiluminescent

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

detection, Analytical Sciences., vol. 19, pp. 557-561, 2003.

[15] C.H. Chiu, Y.H. Sung, S.D. Huang, Simultaneous determination of manganese, iron and cobalt in copper with a multi- element graphite furnace atomic absorption spectrometer, Spectrochimica Acta - Part B Atomic Spectroscopy., vol. 58, pp. 575-580, 2003.

[16] P.H. Lin, K.S.K. Danadurai, S.D. Huang, Simultaneous determination of cobalt, nickel and copper in seawater with a multi-element electrothermal atomic absorption spectrometer and microcolumn preconcentration, Journal of Analytical Atomic Spectrometry., vol. 16, pp. 409-412, 2001.

[17] B. Li, D. Wang, J. Lv, Z. Zhang, Flow-injection chemiluminescence simultaneous determination of cobalt(II) and copper(II) using partial least squares calibration, Talanta., vol. 69, pp. 160-165, 2006.

INTERNATIONAL JOURNAL
FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 ⓒ (24*7 Support on Whatsapp)