



Simultaneous Determination of Cobalt and Iron Made Easy: Results from HPSAM

ARUNA SOLANKI¹, YOGESH KUMAR¹ and NITIN KUMAR^{1*}

Department of Chemistry, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India.

*Corresponding author E-mail: nitinkumar@mlsu.ac.in

<http://dx.doi.org/10.13005/ojc/390230>

(Received: January 04, 2023; Accepted: March 29, 2023)

ABSTRACT

A novel protocol using H-point standard addition method (HPSAM) has been developed for simultaneous determination of cobalt and iron metals. We have herein focused on measurement of concentration of an analyte (cobalt) in the presence of other serving as the interfering species (iron). 4-[3-hydroxy-3-(4-methylphenyl) triaz-1-ene-1-yl] benzene sulfonamide (HTSN) was employed as the reagent in the presence of Triton x-100 which served as surfactant). The analytical signals were measured using two different wavelengths, λ_1 (390) and λ_2 (418). The analytical utility of adopted method has been tested and verified under the optimized conditions such as-pH of the medium, colour development of complex and reagent concentration etc. The molar absorptivity was found to be 74413 and 41691 L mol⁻¹ cm⁻¹ with excellent root mean square value 0.9992 and 0.9984 for Co (II) and Fe (III), respectively. The RSD values were 1.01 and 2.56 for Co and Fe, respectively. The whole methodology is simple, rapid and cost effective. We have successfully applied this method the analysis of Co (II) and Fe (III) in synthetic samples.

Keywords: Spectrophotometric determination, HPSAM, Cobalt, Iron, HTSN, Analytical.

INTRODUCTION

Iron and cobalt metals have some similar chemical behavior and appear together or alone in many environmental and biological samples, especially in alloys. Iron is an essential element required for proper functioning of numerous metabolic activities like oxygen transport, enzyme activity, regulation of cell growth and differentiation¹. On the other hand, cobalt is an essential microelement and the only metal found in vitamins (Vitamin B12)². Cobalt compounds are efficient catalysts and are often used in a number of industrial processes. A

number of methods have been projected for the simultaneous determination of different metal ions like derivative spectrophotometry³, atomic emission spectrophotometry⁴, H-point standard addition⁵⁻¹⁰ and the partial least square method¹¹⁻¹³.

H-point standard addition method (HPSAM) was developed way back in the year 1988, by Bosch-Reig and Compins-Falco¹⁴⁻¹⁶ for simultaneous determination of metals. It is a simple bivariate chemometric technique based on dual wavelength spectrophotometry and modification of standard addition method¹⁷⁻²⁰. This method is advantageous



owing to its ability towards removal of both proportional and constant error, produced by the sample matrix²⁰⁻²². Besides, it offers better resolution of the overlapping spectra of metal complexes²³. This method enables calculation of concentration of one species in the presence of other interfering species²⁴. Thus, the aim of the present paper is to find out the possibilities of spectrophotometric methods for simultaneous determination of Co(II) and Fe(III) with synthesized chromogenic reagent in aqueous media via HPSAM.

In the present method, two wavelengths were selected to measure different analytical signals of analyte and interfering species^{25,26}. Under such optimized conditions, a calibration graph was constructed according to the standard addition method. The calibration lines for both the selected wave-lengths crossed at a point, called the H-point which indicated the additive effect of analyte and interferent concentration.

Here in, we report the determination of Co(II) and Fe(III) simultaneously using chromogenic reagent 4-[3-hydroxy-3-(4-methylphenyl) triaz-1-ene-1-yl] benzene sulfonamide (HTSN). The versatility of the developed method was further explored with synthetic solutions.

MATERIALS AND METHOD

Materials

All chemicals used were of analytical grade and were employed directly without any further purification. Double distilled water was utilized throughout the work. Stock solutions of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3$ were prepared in 100 ml volumetric flask and a few drops of conc. H_2SO_4 and conc. HNO_3 , respectively, were added to prevent hydrolysis. Both solutions were subsequently standardized. Perchloric acid and Tris buffer solutions were used for adjusting the pH. The entire work was carried out using HTSN chelating reagent and Triton X-100 and all solutions were freshly prepared as per the need.

Apparatus

An Elico SL-210 double beam UV-Vis spectrophotometer was used for analyzing the spectrophotometric work and 1 cm quartz cuvettes were employed for absorbance measurements. Absorbance spectra were recorded in the range

350-600nm. The pH measurements were carried out using CHEMLINE Digital pH meter with ATC CL 120 (with combined glass electrode).

Methods

Preparation of HTSN Reagent

This method includes coupling of aryl hydroxylamine with diazonium salt of sulfanilamide in acetate buffer medium at pH5-6 with temperature between 0-5°C. The products of the coupling reaction were washed with distilled water and recrystallized using ethanol as solvent. Pale yellowish crystals of hydroxytriazene was obtained. The purity of the compound was checked using thin-layer chromatography (TLC) and melting point detection. The characterization of the compound was pursued with FT-IR, ¹H NMR and mass spectra.

General Procedure

The entire experiment was conducted using standard solutions of Co(II) and Fe(III) ions. Aliquots of varying concentration of Co(II) and Fe(III) with 5 mL of 1×10^{-3} M HTSN solution, 2.0 mL of Triton X-100 (10% v/v, surfactant to solubilize the reagent) and 2.0 mL of Tris buffer (1%) were taken in a 10 mL volumetric flask. The volume of the solutions was made up to the mark with double distilled water and was left for at least 10 min at 25°C. The absorption spectra were recorded at 406 and 395nm wavelength against reagent blank for the individual calibration of Co(II) and Fe(III).

H-point standard addition method

All steps of the HPSAM procedure were performed in a systematic way. During the first stage of the procedure, mixtures of synthetic solutions with different concentration were prepared from standard solutions of cobalt and iron. Further, 0.4 mL of synthetic mixtures, 5 mL of HTSN reagent, 2 mL of tris buffer (1%) and 2 mL of triton X-100 (10%) with subsequent standard additions of additive Co(II) ranging from 1×10^{-5} to 5×10^{-5} were taken in a 10 mL volumetric flask and the solutions were diluted with double distilled water. The solutions, thus obtained had varying concentration of Cobalt, while the concentration of iron was kept constant. The samples were dispensed to a quartz cell and the absorbance was measured at the two selected wavelengths mentioned in HPSAM system.

For preparing the H-point graph, the absorbance data obtained at the two selected wavelength (λ_1 and λ_2) were used with the standard addition of Co(II) concentration solution. The two straight lines were plotted for absorbance and concentration, both derived lines were allowed to cross at a point by extrapolation, and the intersection point of these two lines was termed as CH and AH respectively. The Co(II) ion concentration was evaluated from CH and the concentration of Fe(III) was evaluated from AH.

RESULT AND DISCUSSION

The simultaneous determination of Co(II) and Fe(III) with reagent in the presence of Triton

X-100 by the use of suggested method has been performed. All the work was carried out in micellar media, which solubilized the insoluble component in water and also aided in eliminating the extraction step using organic solvent.

Characterizations of HTSN Reagent

Pale yellow crystals, m.p. 160°C; FT-IR: O-H (3566 cm^{-1}), N-H₂ (3227 cm^{-1}), N=N (1426 cm^{-1}), C=N (1317 cm^{-1}), S=O(1160 cm^{-1}). ¹HNMR: δ (ppm)=2.40 (s,3H), 3.35 (s,2H), 12.21(s,1H), 7.37-7.99 (m,8H). ¹³CNMR: δ (ppm) 20.67, 114.47, 119.75, 127.23, 129.65, 137.29, 140.12, 140.26, 143.26. Mass(m/z): (C₁₃H₁₄N₄O₃S) cal. 306.34; found 307.34. The acquired spectra are shown in Fig. 1(a) IR, (b) NMR (i) ¹HNMR, (ii) ¹³CNMR (c) Mass.

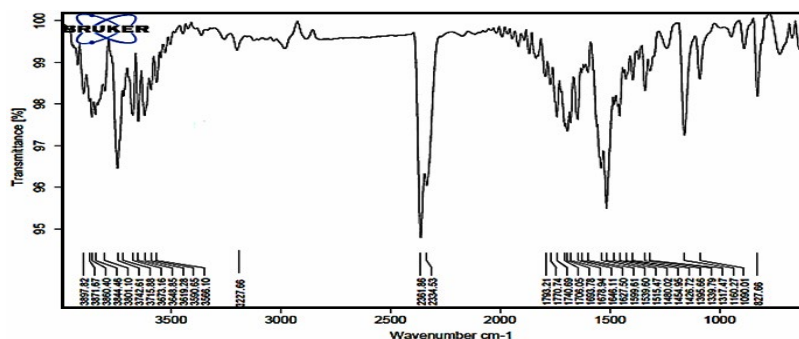


Fig. 1(a). IR Graph of HTSN

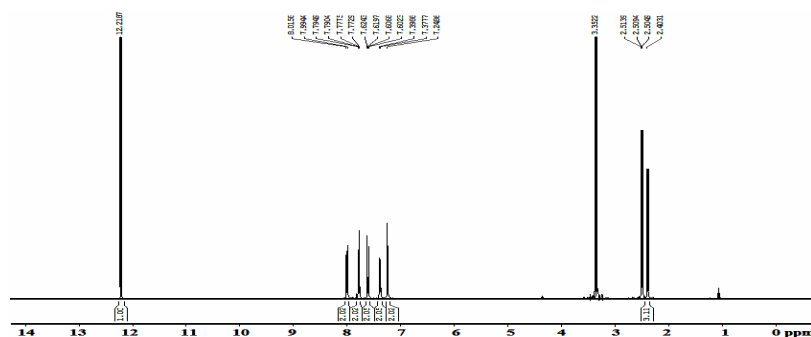


Fig. 1(b). (i) ¹HNMR Graph of HTSN

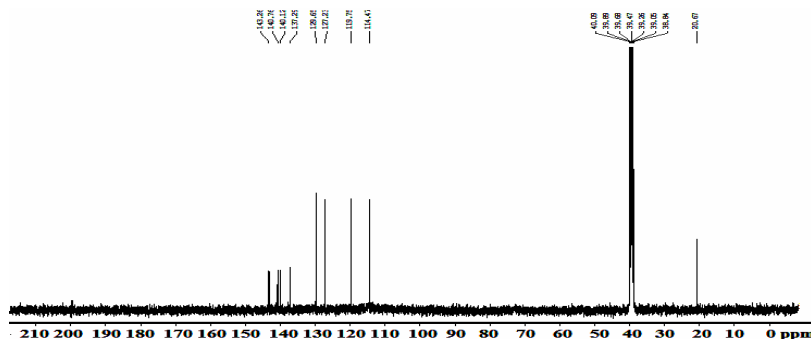


Fig. 1(b). (ii) ¹³CNMR Graph of HTSN

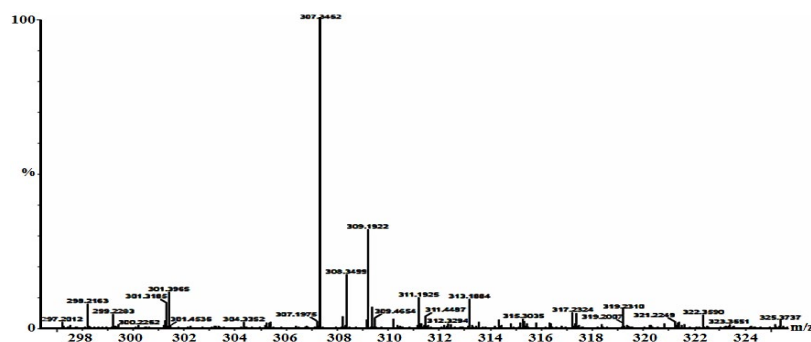


Fig. 1(c). MASS Graph of HTSN

Individual calibration

Hydroxytriazene is an excellent chelating agent. Hence, the present work describes simultaneous determination of Co(II) and Fe(III) using hydroxytriazene by HPSA method. The entire metal determination procedure was performed using UV-spectrophotometer under optimal conditions. Individual calibration of Co(II) and Fe(III) with reagent were measured in the wavelength range 380 to 600nm against reagent blank solution. The wavelength at which maximum absorbance was observed, selected as the working λ_{\max} for individual binary complex. The working wavelength in this case for Co(II) was 402.5nm and for Fe(III), it was found to be 395nm. HTSN reagent forms colored complexes with Co(II) and Fe(III). It was observed that complexation reaction of Co(II) with the ligand HTSN was faster than that of Fe(III) under same conditions. The absorption spectra for the individual colored Co(II)-HTSN and Fe(III)-HTSN complexes overlapped with each other, which was not suitable for the spectrophotometric measurements of the ions. Since the spectra overlapped, Co(II) and Fe(III) could not be determined simultaneously. To address this issue, HPSA method was used as an accurate and simple method for simultaneous determination of both metals. The absorption spectra of Co(II) and Fe(III) complexes with reagents are shown in Figure 2.

Effect of pH

The influence of the medium pH on spectra of complexes of Co(II)-HTSN and Fe(III)-HTSN is the most significant parameter for further study. pH study was carried out using perchloric acid and tris-buffer in the pH range of 3-10 as shown in Fig.3. It was observed that analytical signals varied with pH. Absorbance of Fe-hydroxy complex increased till pH 7, after which the absorbance decreased, whereas the Co complex showed maximum absorbance within 7 to 9 pH range. Therefore, a pH range of 7-8 was selected for further study.

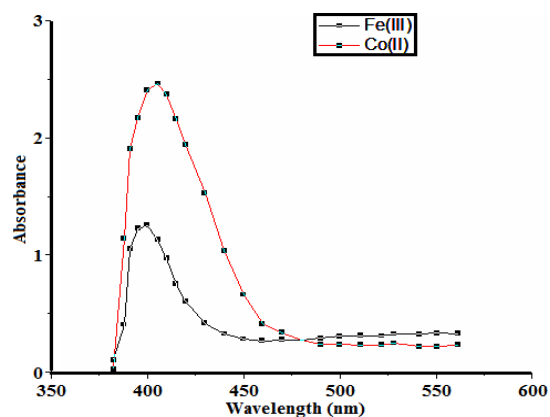
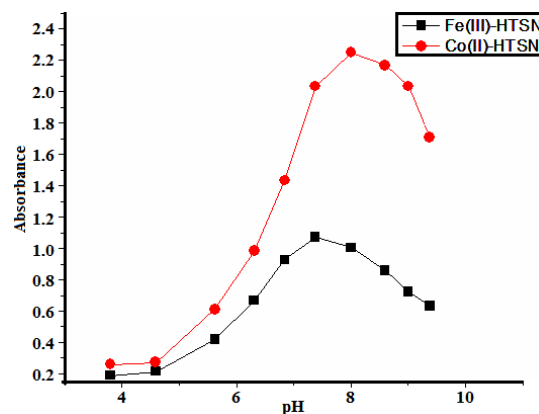
Fig. 2. Absorption spectra of Co(II)-HTSN complex ($C_{Co} 5 \times 10^{-5}$, CHTSN 5×10^{-4}) and Fe(III)-HTSN complex ($C_{Fe} 5 \times 10^{-5}$, CHTSN 5×10^{-4}).

Fig. 3. Effect of pH on absorption spectra of Co(II)-HTSN and Fe(III)-HTSN complex

Effect of surfactant

Since, the obtained complexes were insoluble in water, Triton X-100 was selected as the working micellizing agent to dissolve the insoluble part in water. The effect of surfactant on optimum absorbance of Co(II) and Fe(III) complexes was studied. The obtained results revealed that the

absorbance of the solutions increased upon usage of surfactant and it also increased the solubility and stability of the complexes in aqueous media.

Validation of Beer's law

For the validation of Beer's law, sixteen set of each binary complex of Co(II) and Fe(III) with reagent at variable concentration in 1:10 ratio were prepared under optimized conditions and absorbance at selected wavelengths were recorded. The results have been presented in Fig. 4. It was observed that the absorbance increased with the increase in concentration of reagent. Thus, the exact concentration of reagent with Co(II) and Fe(III) was used for the study of HPSAM.

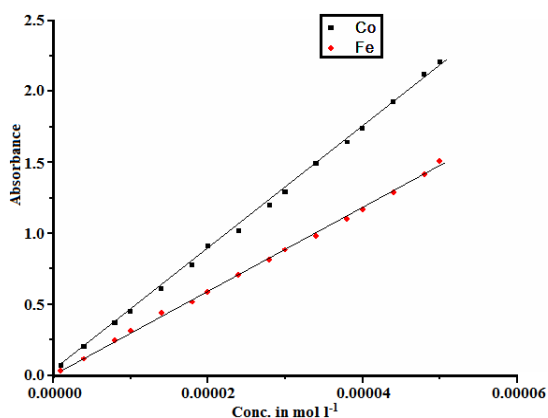


Fig. 4. Calibration curve of Co-HTSN at 406nm & Fe-HTSN complex at 395nm

H-point standard addition method

The selection of two wavelengths λ_1 and λ_2 were the main requirements for HPSAM. The essential condition is that absorbance of analyte must be linear with concentration and the interfering signal must remain unaffected with change in analyte concentration. The analytical signal of mixture which contain analyte and interfering species should be equal to the sum of the individual signals of the two compounds, the difference in the slopes of the two straight lines should be as large as possible to get good accuracy. In the proposed method, Co(II) and Fe(III) ions were used as analyte and interfering species, respectively. A known concentration of Co ion was consecutively added to the mixture, after the addition of analyte and the absorbance was measured at selected wavelength ($\lambda_1=390$ and $\lambda_2=418$ nm) against reagent blank. As mentioned above in Fig. 1, at the two selected wavelengths, the Co(II)-HTSN complexes signal increases linearly with the addition

of various concentration of Co analyte, whereas the signals of Fe(III) do not change. The Co(II) ion concentration was determined by the HPSAM. These can be expressed by following equations.

$$A_{390} = M_{390}C_{Co} + b_o + b \quad (1)$$

$$A_{418} = M_{418}C_{Co} + A_o + A \quad (2)$$

Where, A_{390} and A_{418} are the two analytical signals, two straight lines obtained intersect at H-point ($-C_{Co}, A_{Fe}$), shown in Figure 5.

The Co ion concentration was calculated by HPSAM system using the equation of two straight lines, whereas the concentration of Fe was determined by the analytical signal from the calibration graph as shown in Figure 4.

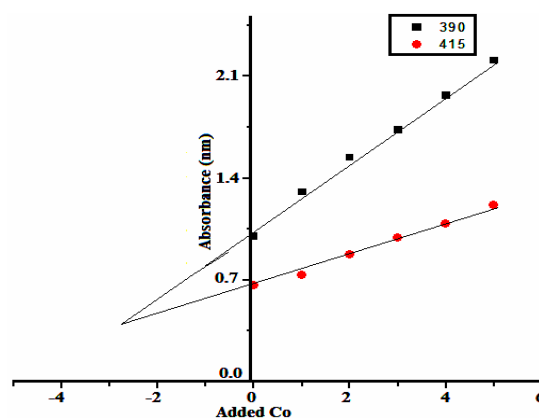


Fig. 5. HPSAM plot for simultaneous determination of cobalt and Iron under optimized Condition with a C_{Co} 2.66×10^{-5} and C_{Fe} 1.33×10^{-5} at selected wavelength $\lambda_1=390$ and $\lambda_2=418$ nm

Reproducibility of the method

To investigate the reproducibility and success of this method, total five replicate samples were prepared for determination of Co(II) and Fe(III) with the addition of analyte concentration. The binary mixture solution was poured into a 1 cm quartz cuvette and the spectra were screened at selected wavelength. The analytical results obtained from HPSAM were checked and tested by the repeatability of the process. The temperature was kept constant while performing the spectrophotometric work.

HPSAM graph was constructed with the data obtained from spectroscopic studies. It was observed that the standard addition of Co metal ion concentration

is the key step of HPSA Method. Molar absorptivity, linear range and root mean square value described in Table 1 were calculated from the calibration curve, whereas Table 2 shows the reproducibility and success of the present method, as well as the mean, and RSD values. The relative standard deviations 1.01% and 2.56% were obtained for Co and Fe, respectively. The results for both metals, therefore, indicates the success of HPSAM technique.

Table 1: Statistical analysis of Co(II) and Fe(III)

Parameters	Co(II) at 418nm With Triton X-100	Fe(III) at 390nm With Triton X-100
Molar absorptivity (L mol ⁻¹ cm ⁻¹)	74413.38	41691.44
R ²	0.99928	0.99841
Linear range (mol L ⁻¹)	6×10 ⁻⁶ to 5×10 ⁻⁵	6×10 ⁻⁶ to 5×10 ⁻⁵

Table 2: Results of Five replicate simultaneous determination of Cobalt and Iron

Expected concentration (mol L ⁻¹)		Obtained concentration (mol L ⁻¹)	
Co(II)	Fe(III)	Co(II)	Fe(III)
2.66×10 ⁻⁵	1.33×10 ⁻⁵	2.67×10 ⁻⁵	1.28×10 ⁻⁵
2.66×10 ⁻⁵	1.33×10 ⁻⁵	2.66×10 ⁻⁵	1.31×10 ⁻⁵
2.66×10 ⁻⁵	1.33×10 ⁻⁵	2.69×10 ⁻⁵	1.35×10 ⁻⁵
2.66×10 ⁻⁵	1.33×10 ⁻⁵	2.72×10 ⁻⁵	1.33×10 ⁻⁵
2.66×10 ⁻⁵	1.33×10 ⁻⁵	2.64×10 ⁻⁵	1.38×10 ⁻⁵
Mean	2.676×10 ⁻⁵	1.33×10 ⁻⁵	
S.D.	2.727×10 ⁻⁷	3.405×10 ⁻⁷	
R.S.D.	1.01%	2.56%	

CONCLUSION

The proposed method was established

for the simultaneous determination of Co and Fe. In addition, to check the accuracy of this method several synthetic samples were prepared with different concentration of Co ion and the spectra of both complex (Co(II)-HTSN and Fe(III)-HTSN) were plotted simultaneously at selected wavelength (λ_1 and λ_2) as shown in Fig. 4. The results obtained from the sample containing the interfering ion varied from each other, so two calibration graphs were intersected at a common point (H-point) and it provided sufficient data for reliable determination of Co(II) and Fe(III). Thus, HPSAM shows satisfactory analytical results for the simultaneous determination of Co and Fe using HTSN reagent in aqueous medium and the developed method is simple, cost effective, rapid and precise. However, to enhance the reproducibility, the same process could be repeated with different synthetic ligands.

ACKNOWLEDGMENT

The authors are thankful to the Coordination Chemistry Lab, Department of Chemistry, MLSU University, Udaipur, India. We extend special thanks for the characterizations studies like NMR at SAIF, Punjab University Chandigarh, India, MASSat MNIT, Jaipur and FTIR at the Coordination Chemistry Lab, Department of Chemistry, MLSU University, Udaipur, India.

Conflict of Interest

The authors declare that there is no conflict of interest.

REFERENCES

- Nekouei, S.; Nekouei, F.; Ulusoy, H. I.; Hossein, N., *Desalin Water Treat.*, **2015**, *57*, 1–10.
- Moghadam, M. R.; Jahromi, S. M. P.; Darehkordi, A., *Food Chem.*, **2015**, *192*, 424-431.
- Varghese, A.; Khadar, A. M. A.; Kalluraya, B., *Spectrochimica Acta Part A*, **2006**, *64*, 383–390.
- Brykina, G. D.; Kozyreva, G. V.; Khlystova, A. D.; Yu, S. N. Zh., *Anal. Khim.*, **1985**, *40*, 1925-1929.
- Pouretedala, H. R.; Asefi, M., *J. Iran. Chem. Soc.*, **2007**, *4*(4), 503-509.
- Muhammad, W. S.; Diyar, S. A., **2022**, *99*(7), 100526.
- Hayam, M. L.; Sarah, S. S. C.; El-Maraghye, M., *Spectrochim Acta Part A: Molecular and Biomolecular Spectroscopy*, **2020**, *224*(5).
- Modawe, N. M.; Eltayeb, M. A. Z. *Adv Anal Chem.*, **2013**, *3*(1), 1-7.
- Ahmadi, F.; Saraskanrood, F. B. *Electro analysis.*, **2010**, *22*(11), 1207-1216.
- Kaur, V.; Malik, A. K.; Verma, N., *Turk J Chem.*, **2010**, *34*, 295–305.
- Safavi, A.; Abdollahi, H.; Mirzajani, R., *Petrochimica Acta Part A*, **2006**, *63*, 196–199.
- Gao, L.; Ren, S., *Spectrochimica Acta Part A*, **2005**, *61*, 3013–3019.
- Ghasemi, J.; Nikrathi, A.; Niazi, A., *Turk. J. Chem.*, **2005**, *29*, 669–678.
- Reig, F. B.; Falco, P. C., *Analyst.*, **1988**, *113*, 1011-1016.

15. Falco, P. C.; Reig, F. B.; Benet, A. M., *Fresen J Anal. Chem.*, **1996**, *338*, 16-21.
16. Reig, F. B.; Falco, P. C., "Letters", *analyst.*, **1990**, *115*, 111-113.
17. Habibi, Z.; Bamdad, F., *Anal Bioanal Chem Res.*, **2022**, *9*(3), 243-250.
18. Eskandari, H.; Kamali, Y., *Anal Sci.*, **2004**, *20*, 1095-1098.
19. Tu, L. N.; Tan, L. V.; Chien, N. X., *Eur. Chem. Bull.*, **2013**, *2*(6), 311-314.
20. Larionova, E. V.; Bulygina, K. A., *Conf. Ser.: Mater. Sci. Eng.*, **2015**, *81*, 012-093.
21. Reig, F. B.; Falco, P. C.; Andres, J. V.; Legua, C. M., *Talanta.*, **1994**, *41*(1), 39-52.
22. Afkhami, A.; Zarei, A. R., *Anal Sci.*, **2003**, *19*, 9-17.
23. Basher, E. A.; Eltayeb, M. A-Z., *Adv Anal Chem.*, **2014**, *4*(2), 21-29.
24. Mohammadi, S. Z.; Roohparvar, R.; Taher, M. A., *J Anal Chem.*, **2016**, *71*(1), 42-49.
25. Wieczorek, M.; Rengevicova, S.; Wit, P.; Wo niakiewicz, A.; Kozak, J.; Kocielniak, P., *Talanta.*, **2017**, *170*, 165-172.
26. Regar, M. L.; Baroliya, P. K.; Chauhan, R. S.; Goswami, A. K., *Chem. Sci Trans.*, **2016**, *5*(2), 1-7.