

**SPECTROPHOTOMETRIC DETERMINATION OF SULFUR DIOXIDE THROUGH ITS REACTION WITH IODINEMONOCHLORIDE AND PHENOTHIAZINE STABILIZED BY ION-PAIR FORMATION****Lakshmana Beliyaiiah<sup>1</sup>, M Harish Kumar<sup>2</sup> and Suresha M Shivalingaiah<sup>3\*</sup>**<sup>1</sup>Department of Chemistry, Shree Siddeshwara Government First Grade College and PG Studies Center, Nargund, Gadag-582 207, Karnataka, India<sup>2</sup>Department Physics, Government Engineering College, Bedarapura, Chamarajanagar-571313, Karnataka, India<sup>3</sup>Department of Chemistry, Government Engineering College, Kushalnagar, Madikeri-571 234, Karnataka, India

\*Corresponding Author Email: drsoory76@gmail.com

**ABSTRACT**

*In present work we have carried out sensitive spectrophotometric method for the determination of sulphur dioxide involving ion-pair complexation. The developed spectrophotometric method is based on the red chromogenic ion-pair formed by the reaction between chloropromazine and iodine monochloride in hydrochloric acid medium followed by its reduction with sulphur dioxide. The system obeys Lambert-Beer's Law in the concentration range 0.1904 - 4.9504  $\mu\text{g ml}^{-1}$  of sulfur dioxide at 520 nm. Molar absorptivity, correlation coefficient and Sandell's sensitivity values were found to be  $3.0871 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ , 0.99 and  $0.002 \mu\text{g cm}^{-2}$  respectively. Probable reaction mechanisms along with experimental stoichiometry of such ion-pair are indicated. Proposed method was used for the determination of sulfur dioxide content in dried grape sample as well as in air sample.*

*Keywords: Sulfur dioxide; Spectrophotometry; Phenothiazine; Ion-pair*

**INTRODUCTION**

Sulfur dioxide is a major pollutant that has been causing environmental concern over recent decades [1]. Industrial emissions and other urban air pollutants pose a major threat to human health. Sulfur dioxide, ( $\text{SO}_2$ ), is a common pollutant of urban air [2]. It is widely used as an antioxidant in the pharmaceutical industry [3-4] as a bleaching agent in the paper and pulp industries [5] and also as a food preservative and refrigerant [6-7].

As a matter of growing concern for sulfur dioxide as an air pollutant, there appears to be an upsurge in the interest of developing various methods [8] for its quantitative determination, such as for example, titrimetry [9], spectrophotometry [10], chemiluminescence [11], chromatography [12], fluorimetry [13], flow injection analysis [14] and also polarography [15] which are particularly used for the determination of sulfur dioxide in air, sugar [16], wines [15] and beverages [11].

Among such methods, spectrophotometric method [17], rosoline is used as a reagent, which is considered to be toxic [18] and also requires the reagent contained in a brown bottle to be stored in a refrigerator. In one of the spectrophotometric method [19] requires extraction step and acidified sulfite solution stabilized by using EDTA. Whereas spectrophotometry, fluorimetry and HPLC [20] are disadvantageous in terms of cost and instruments used in routine analysis. Some of the methods [21] necessitate strict control of  $\text{pH}$  (2- 3.5) and also involving purging [22]. To overcome the above-mentioned limitations; we carried out detailed investigation and developed simple and sensitive spectrophotometric determination of sulfur dioxide through its reaction with iodine monochloride and phenothiazines stabilized through ion-pair formation. The method involving a tested reagent [18], chloramine-T with iodine monochloride is considered to be a superior method over the existing methods. Since the reagent prepared is stable for more than two weeks, it does not require neither strict control of  $\text{pH}$ , nor storage of it in a refrigerator, therefore, the reagent can be applied effectively for the determination of sulfur dioxide. However, the proposed method is a redox reaction and indeed there is interference of the reductants, therefore, interference effect of common air pollutants such as hydrogen sulfide, nitrite and formaldehyde on the determination of sulfur dioxide was studied.

Phenothiazines are a class of heterocyclic compounds and it is the parent of phenothiazine drugs and thiazine dyes [23]. In 1883 Bernthsen synthesized it from diphenyl amine and sulphur [24]. N-alkyl phenothiazines are a class of heterocyclic compounds with low toxicity and good pharmacological activity [25] and finds applications as anti-cholenergic, antihistaminic, antiemetic and antiemetic agents [26]. Phenothiazines in the chemical analysis act as electron donors and normally being oxidized to colored radical cations and thiazones [27], would provide a convenient basis for their kinetic and spectrophotometric studies in the neutral and acidic media of organic solvent systems, involving Ce (IV) and Fe (III) as oxidants [28]. Considering the importance of the phenothiazines in the pharmaceutical industry coupled with their interesting redox behaviour, several analytical methods have been reported for their determination. In the present work, Iodine-monochloride produced using chloramine-T with iodine in acetic acid medium, has been used as an oxidant for the quantitative spectrophotometric determination of sulfur dioxide through its reaction with iodine monochloride and phenothiazines stabilized through the ion-pair formation.

## EXPERIMENTAL

### Materials and Methods

From Sigma-Aldrich Chemicals we were purchased and all the reagents used for the synthesis were of analytical reagent (AR) grade and employed as such until unless specified and water used here refers to distilled water. Spectrophotometer Elico SL 171 (Elico Co India), UV – VIS spectrophotometer (Jena Germany) with 1 cm quartz cells were used for absorbance measurements. High volume air sampler (Micro Neta India) was used for sucking air.

**Standard Sodium Meta-bisulfite Solution:** Weighed amount, 0.1g of sodium metabisulfite was transferred into a 500 ml volumetric flask. It was dissolved and diluted up to the mark with distilled water. Solution was standardized iodometrically and the sulfur dioxide content of the solution was found to be  $120 \mu\text{g ml}^{-1}$

**Chloramine – T:** 1.3868 g of substance was dissolved in 30 ml acetic acid taken in a dry beaker. And 0.3764 g of iodine was taken in a beaker and dissolved it in about 30 ml of acetic acid. Both of these solutions were transferred into a 100 ml volumetric flask and diluted the resulting solution to the mark with acetic acid. When the flask was shaken well a homogeneous yellow solution was obtained, which was further diluted 10 times with acetic acid to use that for the determination of sulfur dioxide.

**Chlorpromazine hydrochloride:** its solution was prepared by dissolving about 0.026 g of the substance initially by adding a few drops of dilute hydrochloric acid and diluted later to 10 ml with water.

### Procedure

A series of labeled 10 ml volumetric flasks were arranged. To each flask 0.4 ml of 0.004289 M chlorpromazine hydrochloride solution, 0.2 ml of 0.0048436 M iodine monochloride reagent was added. Aliquots (0.1-2.6 ml) of sulfur dioxide solution containing about  $0.1904\text{-}4.9504 \mu\text{g ml}^{-1}$  were also transferred, followed by 5 ml of concentrated hydrochloric acid. Then, the solution of each flask was diluted to the mark with water. Absorbance of each test solution and the blank, which was same as that of test solution but not containing sulfur dioxide, were measured against water at 520 nm.

### Determination of Sulfur Dioxide in Dried Grape Sample

In a round-bottomed flask, a known amount of dried grape, 50g, 300 ml of water, 50 ml of 4 M hydrochloric acid were transferred. The condenser was assembled and connected as it was described in an AOAC method [17]. When the solution was started boiling, the heating rate was adjusted to slow boiling and allowed to boil for about 1h. Distilled sulfur dioxide was condensed into the flask, containing 30 ml of water. The total volume of solution so obtained was 380 ml. From that 1 ml aliquot of the solution per trial was examined for sulfur dioxide by the proposed method as well as the official method.

**Determination of Sulfur Dioxide in Air Sample**

A 35 ml of 1.5% triethanolamine solution was transferred into the flask of air sampling apparatus. Air from outside the room was pumped through the flask for four hours at the flow rate of  $1.3 \text{ m}^3\text{min}^{-1}$ . After the termination of the sampling, any loss of trapping solution due to the evaporation was restored to 35 ml by adding 1.5% TEA solution. From that, 1 ml aliquot of the air trapped sample solution, 2 ml of 0.5% sulphamic acid [29] were transferred into a 10 ml labeled volumetric flask and sulfur dioxide content of the flask solution was determined as described in the procedure.

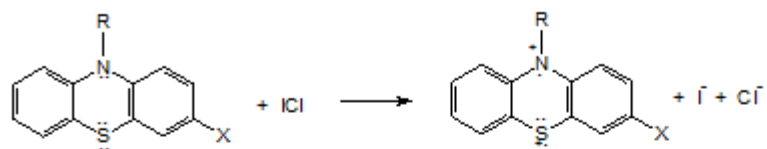
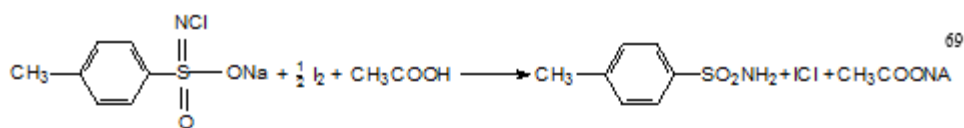
**RESULTS AND DISCUSSION**

Chemical oxidation of phenothiazines is a well known reaction<sup>62</sup> that has been used extensively for their determination [30]. Phenothiazine, chlorpromazine hydrochloride used in the proposed method has produced color radical with the reagent, iodine monochloride in the hydrochloric acid medium. The radical cation of the chlorpromazine,  $\text{Ph}^+$ , is appeared to be associated with a part of the unreacted iodine monochloride [31] in the form of ion – pair,  $[\text{Ph}^+][\text{ICl}_2^-]$ . Addition of sulfur dioxide decreases the color, produced by chlorpromazine with iodine-monochloride [32] system. Decrease in color intensity of the system is found to be a linear function of increasing concentration of sulfur dioxide. This is considered to be due to an electron gain by chlorpromazine radical cation the linear decrease in absorbance of the system was measured at 520 nm. The system obeys Lambert–Beer’s law, Fig.1, for the determination of sulfur dioxide in the concentration range  $0.1904\text{--}4.9504 \mu\text{g ml}^{-1}$ . The system produced a straight line with slope,  $-0.136$  and intercept  $0.95$ . Molar absorptivity, correlation coefficient and Sandell’s sensitivity values were found to be  $3.0871 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ,  $0.99$  and  $0.00207519 \mu\text{g cm}^{-2}$  respectively.

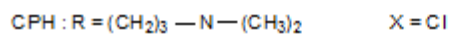
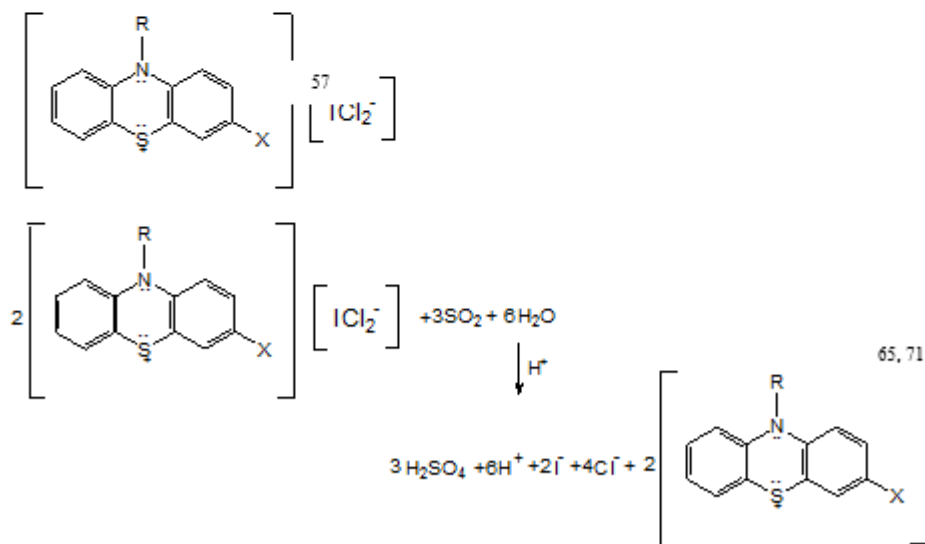
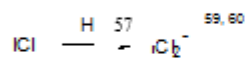
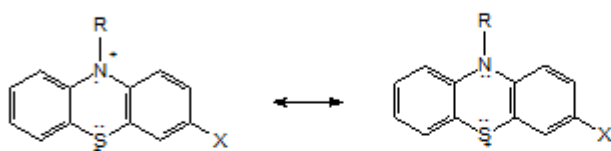
The proposed method is based on the ion-pair formation between chlorpromazine and iodine monochloride in hydrochloric acid medium producing red color followed by its reduction with sulphur dioxide. Stoichiometric composition of chlorpromazine to iodine monochloride was determined by Job’s modified method and the experimental procedure that was followed is as indicated in Table 1. The graphical representations of those results are shown in Fig. 2, which are accounting for 1:2 stoichiometry between chlorpromazine and iodine monochloride. The stability constant value was also calculated, Table 1, for the system by Turner and Anderson’s method and it was found to be  $1.58487 \times 10^5 \text{ mol}^{-1} \text{ L}$ .

The amount of sulfur dioxide present in dried grape, air samples and sodium metabisulfite solutions was determined. Results obtained were reproducible with standard deviation  $0.01\text{--}0.058$  and relative standard deviation  $0.09\text{--}3.21\%$ . For a comparison of results, the sulfur dioxide contents in those samples were also determined separately following the AOAC method [AOAC method involves sodium metabisulfite, sodium tetrachloromercurate, rosaniline and formaldehyde solution. Measures absorbance at 550 nm. The results so obtained by both the methods agree with one another.

Reaction Mechanism



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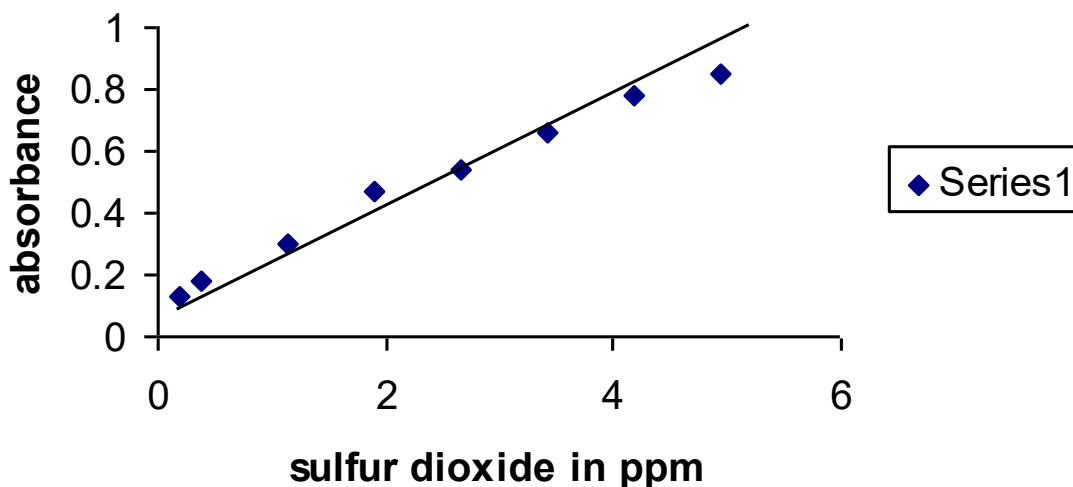


Fig.1. Calibration graph

\*Absorbance = Absorbance of blank solution - Absorbance of test solution

**Table 1:** Job's modified method for phenothiazine- iodine monochloride complex

Vol.of 0.001M chlorpromazine solution in ml	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Vol. of 0.001M iodine monochloride solution in ml	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
Absorbance	0.453	1.229	1.823	1.920	1.958	1.795	1.508	1.267	0.829

1. Here 10 ml volumetric flasks were used and the solutions were diluted to mark with concentrated hydrochloric acid and absorbance was measured at 520 nm.

**Table 2:** Job's modified method for phenothiazine- iodine monochloride complex

Vol.of 0.001M chlorpromazine solution in ml	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Vol. of 0.001M iodine monochloride in ml	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
Absorbance	0.111	0.428	0.600	0.688	0.690	0.609	0.469	0.370	0.301

2. Here 25 ml volumetric flasks were used and the solutions were diluted to mark with concentrated hydrochloric acid and absorbance was measured at 520 nm.

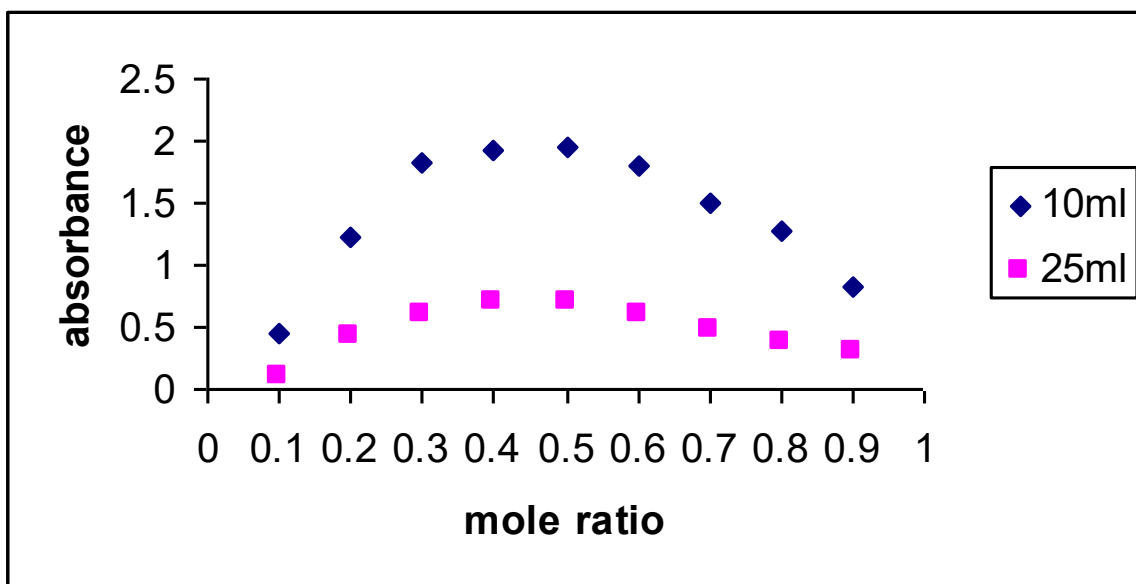


Fig. 2. Determination of stoichiometry and stability constant by Job's method

Table 3: Determination of sulfur dioxide in different samples of dried grape and air sample.

Samples	Concentration of Sulfur Dioxide**		t-test***	F- test***
	Proposed method $\mu\text{gml}^{-1}$ ( $\pm$ SD)	Official method in $\mu\text{gml}^{-1}$ ( $\pm$ SD)		
Dried grape	0.27( $\pm$ 0.27)	0.29( $\pm$ 0.28)	1.76	1.07
Air sample	1.75( $\pm$ 0.05)	1.78( $\pm$ 0.04)	1.14	2.32

\* Dried grape from local market.

\*\* Sulfur dioxide  $\mu\text{g ml}^{-1}$  is a mean value of five determinations.

\*\*\* Tabulated values 95% confidence limit is (2.776) and (6.59) for t and F- tested respectively.

#### Effect of Acids on the Color Stability of the Chlorpromazine

In an attempt to understand the effect of acids on the color stability of the chlorpromazine with iodine monochloride system, 0.4 ml chlorpromazine hydrochloride ( $4.289 \times 10^{-3} \text{M}$ ) was pipetted into a 10 ml volumetric flask. To that flask a measured volume, 0.2 ml iodine monochloride reagent was added. The resulting solution was diluted to the mark with 5 M sulfuric acid, or 3 M hydrochloric acid, or acetic acid (Glacial), or 20 M sulfuric acid or 11 M hydrochloric acid. The solutions of chlorpromazine hydrochloride have produced color with the iodine monochloride reagent but the color intensities of the solutions were found to increase upon their dilution with the acids. The color intensities of the solutions which were diluted with 5 M  $\text{H}_2\text{SO}_4$ , 3M HCl and acetic acid were observed to be having lower intensities (5 M  $\text{H}_2\text{SO}_4$   $0.707 \times 10^3$ , 3 M HCl  $1.09 \times 10^3$  and  $\text{CH}_3 \text{COOH}$   $0.778 \times 10^3$ ), but the solutions that were diluted with 20 M  $\text{H}_2\text{SO}_4$  and 11 M HCl were found to be having higher intensities (20M  $\text{H}_2\text{SO}_4$   $6.12 \times 10^3$ , 11M HCl  $4.85 \times 10^3 \text{ L Mol}^{-1} \text{ cm}^{-1}$ ). The color intensities of the solutions which were diluted with first three acids were observed to be decreasing gradually with time and finally discharged their color completely in about 2h. But color intensities of the solutions which were diluted with last two acids were found to be of equal and their color persisted even after 24h. Therefore, the reaction mixtures of the chlorpromazine were diluted with concentrated hydrochloric acid while determining sulphur dioxide present in the various samples analyzed.

### Interference Effect

Tolerance limit of the common air pollutants namely, hydrogen sulfide, nitrite and formaldehyde on experimental solution containing  $1.14 \mu\text{g ml}^{-1}$  of sulfur dioxide was tested by studying the effect of those on the absorbance of the experimental solution. The maximum tolerance limit values which were observed are given in the Table 3. Nitrite was found to be not interfering up to  $0.334 \mu\text{g ml}^{-1}$  concentration. At a higher level of its concentration, there was found to be a decrease in absorbance values. However, its interference up to  $10.672 \mu\text{g ml}^{-1}$  had effectively overcome, Table 3, by the addition of 0.5 ml of 0.5% sulfamic acid to the sample solution before its analysis for sulphur dioxide.

**Table 4.** Effect of interference on the determination of sulfur dioxide

Interferant added	Tolerance Limit $\mu\text{g ml}^{-1}$
H <sub>2</sub> S(Na <sub>2</sub> S)	0.6572
NO <sub>2</sub> <sup>-</sup> (NaNO <sub>2</sub> )	0.334
HCHO	100.0

### APPLICATION

The Proposed method was used for the determination of sulfur dioxide content in dried grape sample as well as air sample. The respective average sulfur dioxide contents in those samples were found to be  $26.6 \text{ mg kg}^{-1}$  and  $1.56 \text{ mg ml}^{-1}$ .

### CONCLUSIONS

Described method is simple, rapid and found to be sensitive for the determination of sulfur dioxide. Under the specified experimental condition and at fixed concentrations of chloro-promazine and iodine-monochloride, the amount of sulfur dioxide present in the samples was found to be directly proportional to the decrease in color intensity of the ion-pair system. A simple, sufficiently stable, highly sensitive and most affordable colorimetric method for the determination of sulphur dioxide through its reaction with iodine monochloride and phenothiazine stabilized through ion-pair formation in the dried grape sample as well as air sample is described successfully. Therefore, the present method could be an alternative or a complementary one to an official method for the determination of sulfur dioxide.

### REFERENCES

1. K.Geetha, N. Balasubramanian, *Microchem. J.* **65**, 45, 2000.
2. Y. Alarie, C.E Ulrich, W.M Busey, A.A Krumm, H.N MacFarland, C. Va Falls,. *Arch Environ. Health.* **24**, 115, 1972.
3. G. L.Jenkins,,D. E.Francke, E. A.Brecht, G.Sperandio., *The Art of Compounding*, the Blakiston Company, Philadelphia, Pennsylvania, pp 462, 1951.
4. L. C. Schroeter, J.Phason, *Science*, **50**, 891, 1961.
5. E.Meyer, *Chemistry of Hazardous Materials*, 2<sup>nd</sup> Edn, Prentice-Hall. Inc., Upper saddle River N.J., pp 106, 1989.
6. N. N.Green wood, A. Earnshaw, *Chemistry of the Elements*, Pergamon press, oxford, U.K. pp 824, 1989.
7. H. Seger, K.Clarck, *Chem., ztg.*, 1931, **55**, 838. *Chem.Abstr.* **26**, 774, 1932.
8. F. Solynosi, A. Varga,. *Anal. Chem. Acta*, **17**, 608, 1957.
9. L. Marsos, *Magyar Kem, M.K.Folyoirat*, 1958, 64, through *Chem. Abstr.*, 52, 11661f 1958.
10. A.H.Laila, *Talanta* **36**, 445, 1989.

11. H. Meng, F. Wu. Z. He. Y. Zang ,*Talanta*, **48**, 571, 1999.
12. I I M Elbeih,. G.C .Gabra , *Chem. Anal.*, **52**, 36, 1963.
13. G.Guoquam, He. X. Heraigong. W. *Anal. Lett.*, **28**, 909, 1995.
14. C.S.Tavares Araccjo, J.Lirade Carvalho, D.Ribeiro Mota, C.L.De Araccjo, N.M.M Coelho. *Food Chem.*, **924**, 765, 2005.
15. P.Bruno, M.Caselli, A.Di fano, A.Traini, *Analyst*, **104**, 1083, 1979.
16. S.K.D.Agarwal, S.K.Upadhayaya, STAI, 44<sup>th</sup> Annual convention, C57 - C87 1980.
17. Official Methods of Analysis of the Association of Official Analytical Chemists 14<sup>th</sup> Ed. Edited by Sydney Williams Published by the AOAC, Inc. Arlington, 201, 1984.
18. The Condensed Chemical Dictionary Ed, G. L. Clark and G. G. Halwley, 8<sup>th</sup> ed. Van Nostrand Reinhold Co. NY, pp 765, 1972.
19. M. K. Bhatt, A. Townshend, *Anal. Chim. Acta*, **55**, 401, 1971.
20. IIM Elbeih, G.C . Gabra, *Chem. Anal.* **52**, 36, 1953.
21. Th. A. Kouimtzis, *Anal. Chim. Acta*, **88**, 303, 1977.
22. James E. Haskins, Henry Kendall, Rodger B. Baird, *Water Research*, **18**, 751,1984. [https://doi.org/10.1016/0043-1354\(84\)90171-4](https://doi.org/10.1016/0043-1354(84)90171-4)
23. V. Raman, Mewa Singh, D. C. Parashar, *Microchemical. J.*, **33**, 226, 1986. [https://doi.org/10.1016/0026-265X\(86\)90059-7](https://doi.org/10.1016/0026-265X(86)90059-7)
24. H.Q. Leo, S.P. Liu, Z.F. Liu, Q. Liu, N.B. Li, *Anal. Chim. Acta*, **449**, 261, 2001.
25. Bernthsen, *Ber. Deut. Chem. Ges.*, **16**, 2896, 1883.
26. M.D.Gowtham, M.S.Yogendra Kumar, M.A.Sathish, Giddappa Nagendrappa. *Arch. Pharm. Med. Chem.*, **337**, 604, 2004. <https://doi.org/10.1002/ardp.200200759>
27. P. C. Huang and S. Gabay, *The Phenothiazines and Structurally Related Drugs* (Eds: I. S. Forest, C. J. Carr, E. Usdin), Raven Press, New York, 1974.
28. M. Tarasiewicz. E. Wolniec, T. H. Puzanovska, *Pharmazie*, **153**, 51, 1998. [https://doi.org/10.1016/S0731-7085\(01\)00520-9](https://doi.org/10.1016/S0731-7085(01)00520-9)
29. N .Gayathri. N.Balasubramniam, *J. of AOAC International*, **84**,1065-69, 2001. <http://dx.doi.org/10.1093/jaoacint/qsad051>
30. K.Basavaiah,. G.Krishnamurthy, *Talanta.*, **47**, 59,1998. [https://doi.org/10.1016/s0039-9140\(98\)00057-5](https://doi.org/10.1016/s0039-9140(98)00057-5)
31. N .Gayathri. N.Balasubramaniyan, *J. AOAC Int.*, **84**(4), 1065, 2001. <https://doi.org/10.1093/JAOAC2F84.4.1065>
32. M.S.Yogendr Kumar, M.D.Gowtham. Mahadevaiah, G.Nagendrappa, *Anal. Sci.* **22**, 757, 2006. <https://doi.org/10.1155/2007/576560>