New Spectrophotometric Determination of Sodium Selenate [Selenium (IV)] and Sodium Selenite[Selenium(VI)] with Iron(II), and Their Quantitative Analysis of Selenium (IV) - Selenium (VI) Present in A Binary Mixtures

Rajkumar Kalaparthi[1]
Department of Engineering Chemistry,
A. U. College of Engineering,
Andhra University, Visakhapatnam – 530 003.
Andhra Pradesh, India;

Srija Korapu[2]
Department of Engineering Chemistry,
A. U. College of Engineering,
Andhra University, Visakhapatnam – 530 003.
Andhra Pradesh, India;

Padmarao Chekuri[3]
Department of organic Chemistry,
Adikavi nannaya university Rajahmundry,
Eastgodavari,533296. Andhra Pradesh, India;

***Abstract*: A new and modern wet chemical method (spectrophotometric) has been developed to determination of selenium by reduction of selenium (IV) and selenium(VI) using iron(II) as a reducing agent in acid medium(phosphoric-hydrochloric acid) at room temperature. The method is capable of determination of selenium from the unknown sample, and the binary mixture analysis also carried out the analyte selenium (IV) and selenium (VI) by the reductant of iron(II). This new spectrophotometric method has not use any different temperature and the reaction carried without using any surfactants. The metal ion in aqueous forms light red colored complex with iron(II), in phosphoric –hydrochloric acid medium showing the maximum absorbance ranging from 395-450nm. Hence, analytical studies were further carried out in between 390nm – 450nm stability of the complex carried out by using absorption spectra, in this reaction absorption spectra play an important role and it give a beauty to the reaction.**

Keywords: - Sodium selenate selenium (IV), sodium selenite selenium(VI), Ferrous ammonium sulphate [Iron (II)] as reductant, determination of selenium, Spectrophotometer

INTRODUCTION.

It is well known that selenium exhibits two stable oxidation states: +4 [selenium(IV)] and +6 [selenium(VI)]. The former can eighter be oxidized to selenium(VI) or reduced to selenium(0) utilizing various oxidizing and reducing agents respectively. But selenium(VI) can only be reduced eighter to selenium(IV) or selenium(0) utilizing only a few reducing agents. Hence more number of methods are available for the determination of selenium(IV) than those of selenium(VI) in literature. In fact the methods for the determination of selenium(VI) are very limited in number.

In the previous chapter, the author has furnished an elaborate discussion for the methods so far available for the determination of selenium(IV). A brief review of the methods and their disadvantages has been mentioned for the sake of continuity and avoiding back reference to the pages. The methods for the determination of se(IV) are abundant and utilized various oxidizing agents[1-13] such as permanganate[1-6], hypochlorite or bromite[7-8], chloramine–T[9], hexacyanoferrate (III)[10,11], periodate[12], bromate[13], etc. In all these methods se(IV) is oxidized to se(VI) the reducing agents[14-33] employed in the determination of se(IV) include diethyl dithiocarbamate[14], hypo[15,16], iodide[17,18], ascorbic acid[19,20], hydrazine[21,22], chromium(II)[23],titanium(III)[24], vanadium(IV)[25],iron(II)[26-29], mercury(I) nitrate[30] , butyl hexyl, or cyclopentyl dithio carbamate[31] etc.In all these methods se(IV) is reduced to elemental se(0). It was earlier mentioned that the end point in these methods was detected either potentiometrically or photometrically, spectrophotometrically or using a redox indicator.

All these earlier methods, as mentioned earlier in the last chapter, suffer from one disadvantage on the other. To mention them briefly, most of these methods are indirect in which se(IV) solution are treated with a known excess of all oxidizing agent or reducing agent (mentioned above) and these excess back titrated with a suitable reagent. Some of these methods require the use of scarcely available or expensive catalyst like titanium(III), osmium tetroxide , iodine monochloride , condensed phosphoric acid , etc… The other methods which utilize the conversional reductants like titanium(III), tin(II), vanadium(IV), chromium(II), ascorbic acid etc., must be carried out at elevated temperatures under inert atmosphere as these reagents are air sensitive. Further, a special apparatus is needed to store these conversional reductants under inert atmosphere to prevent the reagents from aerial oxidation.

The author has also described the recently reported spectrophotometric methods for the determination of selenium(IV) present in tap water[32], sea water[33], waste water[34], soil[35], blood[36] or steel samples[37]. But these methods are found to be cumbersome and expensive because of the exorbitant cost in purchasing the chromogenic reagents and eqipment.

From the discussion presented in the above paragraphs it may be clear that there is no convenient redox procedure or a spectrophotometric method for the determination of selenium(IV), selenium(VI) and for the quantitative analysis of the two ions present in synthetic mixtures. In the present thesis the author has now described simple convenient and accurate spectrophotometric methods for the determination of these ions as well as quantitative analysis of the ions present in the mixtures, using iron(II) as a reducing agent in phosphoric acid medium or phosphoric-hydrochloric acid medium. The details of these investigations have been presented in the subsequent pages.

1. EXPERIMENTAL

1.1 Selenium (IV) solution:

An approximately 0.05M solution of selenium(IV) solution has been prepared from an AR grade sodium selenite (anhydrous) by dissolving the required amount of the salt in distilled water and the solution standardized using a standard solution of permanganate as described by Shrenk and Browning[2]. In the method selenium(IV) solution in 2M sulphuric acid medium also containing 8% disodium hydrogen phosphate are heated to about 90°c in presence of a known excess of permanganate solution and titrated the excess permanganate with iron(II) solution visually or potentiometrically in the normal way. From the solution a 0.02M and a 0.0025M solutions been prepared by suitable dilution to be utilized in the preparation of synthetic mixture [consisting of Se(IV) and Se(VI)] and in the spectrophotometric determinations respectively.

1.2 Selenium (VI) solution

An approximately 0.05M selenium(VI) solution has been prepared from an AR grade sodium selenate(anhydrous) and the solution standardized by titrating against a standard solution of titanium(III) chloride as described ealier[25***]. In the method selenium(VI) solution in 10% hydrochloric acid or sulphuric acid medium is heated to about 80°c and titrated the selenium(VI) potentiometrically against titanium(III) under inert atmosphere at the elevated temperatures. From this, a 0.02M and a 0.0025M solutions have also been prepared by suitable dilution, to be utilized in the preparation of synthetic mixtures and in the spectrophotometric determinations respectively.

1.3 Iron(II) solution:

An approximately 0.60M solution of iron (II)[43] has been prepared from an AR grade ammonium iron(II)sulphate hexahydrate in1M sulphuric acid medium and the solution standardized by titrating against a standard solution of dichromate[45]. In this method iron(II) solution in 1M sulphuric acid and 1M phosphoric acid medium is titrated against a standard dichromate solution using barium salt of diphenyl amine sulphonatre as a redox indicator. From the solution, iron(II) solutions of required strengths have been prepared by suitable dilution.

1.4 Starch solution:

An approximately 20% w/v solution of starch has been prepared and utilized it as a protective colloid in the determination to keep the selenium colloidal particles under suspension in the solution.AR grade syrupy phosphoric and hydrochloric acids have been utilized in this investigation.

2. RECOMMENDED PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM(IV) WITH IRON(II) IN PHOSPHORIC ACID MEDIUM:

To an aliquot (3-12 ml) of 0.0025M selenium(IV) solution taken in a 100ml standard flask, about 70 ml of syrupy phosphoric acid[over all concentration of the acid when the solution is diluted to 100ml is about 10.5M] and 4 ml of starch(20% W/V) solution [which acts as a protective colloid] are added and shaken well. The solution is now treated with required volume of about 0.6M iron(II) solution such that its concentration is about 30 fold in excess to that required for complete reduction of selenium(IV) [se(IV)reduced to se(0)] taken as per the stoichiometric equation . The solution is diluted to the mark. The reaction mixture is occasionally shaken for about 1.15 hours and the absorbance of the solution measured against its corresponding blank at 440 nm. It is compared with the absorbance of the standard calibration curve drawn [between concentration and absorbance] previously using solutions of known concentrations of selenium(IV) in the Beer's law limitations and the amount of selenium(IV) present in the solution is computed. Some of the typical results obtained by this procedure have been shown in table 2.1.

It is contemplated that the highly viscous medium[50], such as phosphoric acid where there is poor transport of the ions, is in general not conducive for the process of crystallization of the selenium colloids. This view is strengthened by the fact that the electron diffraction [shown in figure 2.10] taken from the colloidal particles obtained in 10.5M H_3PO_4 the medium indicate that they were all in the amorphous phase.

Table: 2.1. Spectrophotometric determination of Se(IV) with Fe(II) in H_3PO_4 medium.

S. No	Selenium(IV) found, mg.		Pooled Standard Deviation (sg)	$\frac{(1.96Xsg)}{\sqrt{n}}$	95%Confidence Limits $\bar{x} \pm \frac{(1.96Xsg)}{\sqrt{n}}$
	Reference Method[2].	Author's* Method.			
1	0.5922	0.5963	0.001	0.0008	0.5955-0.5971
2	0.8883	0.8829			0.8821-0.8837
3	1.1844	1.1903			1.1895-1.1911
4	1.4805	1.4745			1.4737-1.4753
5	1.7766	1.7737			1.7829-1.7845
6	2.0727	2.0664			2.0656-2.0672
7	2.2306	2.2373			2.2365 - 2.2381

Absorption spectra of colloidal selenium particles obtained from selenium(IV) with iron(II) in phosphoric – hydrochloric acid medium.

In order to select an appropriate wavelength for the determination of selenium(IV) in phosphoric-hydrochloric acid medium. The author has recorded the absorption spectra of the colloidal selenium particles [overall concentration 0.00034M] obtained by reduction of selenium(IV) with iron(II) in 9.5M phosphoric acid medium[60%v/v] and 1M hydrochloric acid medium. As in the case of the spectra discussed earlier, in this case also the spectra were found to change with respective to shape, λ maximum, and the absorbance value at λ maximum with progress of time.The absorption spectrum of colloidal selenium particles obtained from selenium(IV) [overall concentration 0.00034M] with iron(II) in 9.0M or 60% (v/v) phosphoric acid and 1.0M HCl medium immediately after mixing with 20 fold excess iron(II) has been shown in fig. 2.4 and it may be seen from the figure that it has broad absorption band with λ_{max} at 484nm with an absorbance of 0.757.

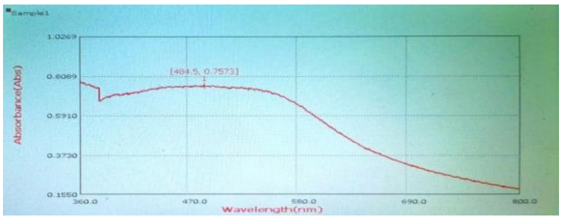


Figure 2.1. Absorption spectrum of colloidal selenium particles obtained from Se(IV) in 9.0M H_3PO_4 plus 1.0M HCl medium [overall concentration 0.00034M] at the onset of reaction.

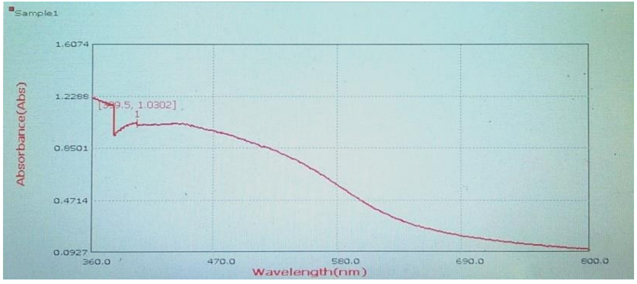


Figure 2.2. Absorption spectrum of colloidal selenium particles obtained from Se(IV) in 9.0M H_3PO_4 plus 1.0M HCl medium after 30 minutes of the reaction.

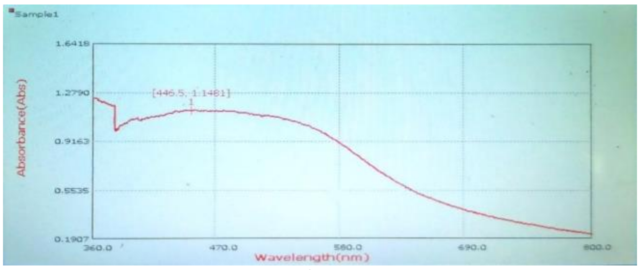


Figure 2.3. Absorption spectrum of colloidal selenium particles obtained from Se(IV) in 9.0M H_3PO_4 plus 1.0M HCl medium after 1hour of the reaction.

3. RECOMMENDED PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM (IV) WITH IRON (II) IN PHOSPHORIC – HYDROCHLORIC ACID MEDIUM.

To an aliquot (3-12ml) of selenium(IV) solution (0.0025M) taken into a 100ml standard flask, required volume of syrupy phosphoric and hydrochloric acid solutions are added such that their overall concentration in 100ml are about 9.0M [60%V/V] and 1.0M [about 9%V/V] respectively. After adding about 4ml of 20%v/v starch solution, the reaction mixture is treated with enough 0.60M iron(II) solution such that its concentration is 20fold in excess to that stoichiometrically required for the complete reduction of selenium(VI) taken, and the solution diluted to the mark. The reaction mixture is occasionally shaken for about one hour. The absorbance of the solution is then measured at 440 nm against its corresponding blank. It is compared with the absorbance of the standard calibration curve drawn [concentration versus absorbance] for selenium(IV) treated under similar conditions and the amount of selenium (IV) present in the solution is computed. Some of the typical results obtained by the above procedure have been presented in table 2.2.

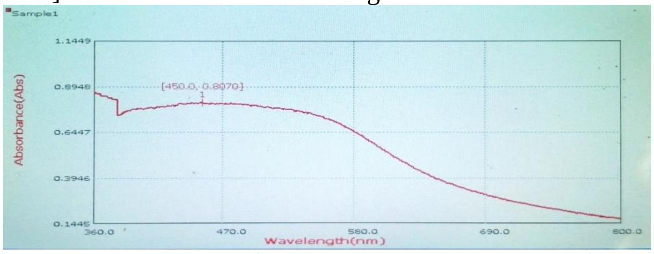
Table 3.1: Spectrophorometric determination of Se(IV) with Fe(II) in H_3PO_4 – HCl medium.

S. No	Selenium(IV) found, mg		Pooled Standard Deviation (Sg)	$\frac{(1.96Xsg)}{\sqrt{n}}$	95%Confidence Limits $\bar{x} \pm \frac{(1.96Xsg)}{\sqrt{n}}$
	Reference Method[2]	Author's* Method			
1	0.6909	0.6975	0.0011	0.0009	0.6966-0.6984
2	0.9870	0.9810			0.9801-0.9819
3	1.2831	1.2895			1.2886-1.2904
4	1.5972	1.5728			1.5719-1.5737
5	1.8453	1.8828			1.8819-1.8837
6	2.1714	2.1648			2.1639-2.1657
7	2.2701	2.2792			2.2783 -.2801

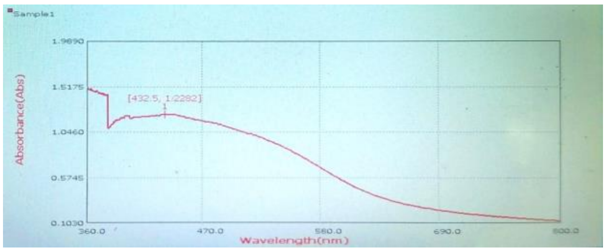
*Average of six determinations.

4. ABSORPTION SPECTRA SELENIUM(VI) WITH IRON(II) IN PHOSPHORIC – HYDROCHLORIC ACID MEDIUM.

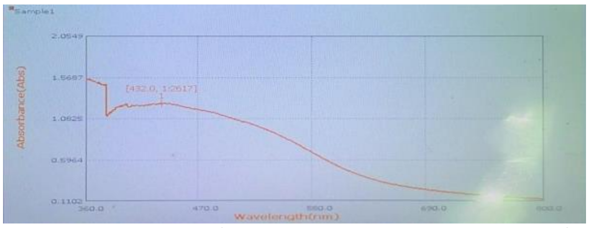
The absorption spectrum of colloidal particles obtained by the reduction of selenium(VI) [overall concentration 0.00037M] immediately after mixing with an excess [40 fold] of iron(II) in phosphoric (9.0M)- hydrochloric acid (1.0M) [catalyzed by chloride ion] medium has been show in figure:4.1



4.1. Absorption spectrum of colloidal selenium particles obtained from Se(VI) [overall concentration 0.00037M] in 9.0M H_3PO_4 plus 1.0M HCl medium at the onset of reaction.



4.2 . Absorption spectrum of colloidal selenium particles obtained from Se(VI) in 9.0M H_3PO_4 plus 1.0M HCl medium after 45 minutes.



4.3 Absorption Spectrum of Colloidal Selenium Particles Obtained from Se(VI) in 9.0M H_3PO_4 plus 1.0M HCl Medium After 1.5 hours.

5. RECOMMENDED PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM(VI) WITH IRON (II) IN PHOSPHORIC – HYDROCHLORIC ACID MEDIUM:

An aliquot (3-12ml) of selenium (VI) solution (0.0025M) is taken into a 100ml standard flask and treated with enough syrupy phosphoric acid, concentrated hydrochloric acid and starch solutions as described above for the determination of selenium(IV) in procedure No. 1.2 . The solution is treated with sufficient volume of abut 0.60M iron(II) solution such that its concentration is 40 fold in excess to that required for complete reduction of selenium(VI) solution taken, as per the stoichiometric chemical equation [pp]. The reaction mixture is occasionally shaken for about one and half hours. The absorbance of the solution is then measured at 440nm against its corresponding blank. It is compared with the absorbance of the standard calibration curve drawn for selenium(VI) treated with iron(II) under similar conditions and the amount of selenium(VI) present in the solution is computed. Some of the typical results obtained by the recommended procedure have been furnished in table 5.1.

Table 5.1. Spectrophotometric Determination of Se(VI) with Fe(II) in H_3PO_4-HCl Medium

S.No	Selenium(VI) found, mg		Pooled Standard Deviation (Sg)	$\frac{(1.96Xsg)}{\sqrt{n}}$	95% Confidence Limits $\bar{x} \pm \frac{(1.96Xsg)}{\sqrt{n}}$
	Reference Method[2]	Author's * Method.			
1	0.7896	0.7943	0.0011	0.0008(8) Or 0.0009	0.7934- 0.7952
2	1.0857	1.0781			1.0772- 1.0790
3	1.3818	1.3887			1.3878- 1.3896
4	1.6779	1.6695			1.6686- 1.6704
5	1.7766	1.7837			1.7828- 1.7846
6	2.0727	2.0664			2.0655- 2.0673
7	2.3688	2.3759			2.3750- 2.3768

*Average of six determinations.

The accuracy of the method is found to be ± 0.7% and the precision of the method is determined by computing the pooled standard deviation and 95% confidence limits to the mean $\bar{x}$ and included these values in the table. These stastistical values indicate that the present method is accurate and precise. Further, the author wish to emphasize that iron(II) is not so far been employed as a reducing agent for the determination of selenium(VI) . The author is first to utilize iron(II) as a reducing agent for the determination of selenium(VI).

6. RECOMMENDED PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM (IV) AND SELENIUM (VI) PRESENT IN A SYNTHETIC MIXTURE.

Synthetic mixture consisting of selenium(IV) and selenium(VI) have been prepared in different 100ml flasks using their respective concentrated solutions(0.02M) such that their total concentrations [Se(IV) and Se(VI) combined together] does not exceed 0.002M when the solution is diluted to 100ml. Five different samples have been prepared in this way.

A 10ml aliquot of a mixture is taken into a 100ml standard flask and the selenium(IV) content determined spectrophotometrically as described in procedure 1.1, by reducing selenium(IV) with iron(II) in 70% phosphoric acid medium [10.5M] alone. In this method selenium(IV) is reduced to selenium(0) while selenium(VI) remains unaffected. Similarly another 10ml aliquot of the same mixture is taken into another 100ml standard flask and treated with 40 fold excess of iron(II) in 9.0 M (60%v/v) phosphoric acid- 1.0M [9%] hydrochloric acid medium and the selenium content determined as described in procedure 1.3. In this method both selenium(IV) and selenium(VI) are reduced to colloidal elemental selenium. Thus, the selenium content obtained in this method corresponds to the total amount of selenium(IV) and selenium(VI) present in the mixture. Upon subtracting selenium content corresponding to selenium(IV), the amount of selenium corresponding to selenium(VI) content can be found, thereby the selenium(VI) content can be found. Some of the typical results obtained by the recommended procedure have been shown in table 6.1.

Table : 6.1 . Quantitative Analysis of Se(IV) – Se(VI) Present in Binary Mixtures.

Sl. No. of Miture	Amount of Se(IV) found in 10ml of the total volume of 100 ml., mg.			Amount of Se(VI) found in 10ml of the total volume of 100 ml., mg.		
	Reference method^2	Present method*	R.S.D %	Reference method^{41}	Present method.	R.S.D %
1	0.4738	0.4766	0.35	1.0265	1.0203	0.23
2	0.6317	0.6285	0.30	0.9159	0.9205	0.26
3	0.7896	0.7828	0.26	0.7422	0.7392	0.31
4	0.9475	0.9437	0.22	0.6159	0.6177	0.36
5	1.1054	1.1087	0.20	0.4738	0.4724	0.38

*****Average of six determinations

The accuracy of the method is found to be ± 0.7%. The precision of the method is found by computing the relative standard deviation%. The values incorporated in the table indicate that the method is accurate and precise.

RESULTS AND DISCUSSION:

From the above furnished experimental part it may be seen that the authors developed new spectroscopic method for the determination of selenium(IV), selenium(VI) and for the analysis of selenium(IV) and selenium(VI) mixture in phosphoric-hydrochloric acid medium using iron(II) as a reducing agent in the results pertaining to these new methods have been presented in table 1.1 - 1.4.From these results it may be seen that selenium(IV) in the case 0.5ml in both the methods 2.0ml selenium(VI) in the range 0.5 to 1.5 can be determined by the method. In the case of selenium (IV) and selenium (VI) synthetic mixture in the range of 0.7 to 1.4 and the latter in the range of 0.5 to 1.1 mg can be determined in the presence of one another. The spectrophotometric method is found to be ± 0.7%.The precision of these methods in the determination of selenium(IV) and selenium(VI) have been computing the pooled standard deviation and 95% confidence limits, while that in the analysis of selenium(IV) and selenium(VI) synthetic mixture it is determined by computing the relative standard deviation percent. All these values have been incorporated in their respective tables from 1.1 to 1.4.

It is well known that iron(II) acts as a reducing agent, it is only a mild reducing agent under normal experimental conditions it is dilute sulphuric or in any other acid medium, but its reducing ability is considerably enhanced in phosphoric acid medium.Gopalrao and co-workers reported that the formal redox potential of iron(II)/iron(III) couple decreases from 0.686v(1M sulphuric acid medium) to 0.400v as the concentration of phosphoric acid increases from 0.0M to 11.0M .In phosphoric acid medium it is expected that iron(III) is bound by $H_2PO_4^-$ ions in the form of a complex causing to decrease the redox potential of iron system and thus enhancing the reducing ability of iron(II) and iron(III).

CONCLUSIONS

In summary, we have introduced a novel convenient and fast approach for the determination of selenium by reducing sodium selenite(Se IV) and sodium selenate (Se VI) using iron (II) as a reductant in 9M phosphoric and 1M hydrochloric acid medium. This method is simple and inexpensive for determination of selenium present in unknown sample and the binary mixture analysis also carried out by using the spectrophotometric determination technique.

ACKNOWLEDGMENTS

The authors are grateful to the authorities of Andhra university for the research facilities provided for undertaking the work, and Dr.B.Kishore Babu for the work done on spectral data analysis. Further, the authors wish to thank the Authorities of department of engineering chemistry A. U. College of Engineering (A), Andhra University for carryout this research.

REFERENCES:

[1] Marino.L.,Z.anorg.chem.,65.32;Cf: chem.Abstr.,4,556(1910)
[2] Schrenk, W.T. and Browning, B.L.,J.AmChem.Soc,48,2550(1926).
[3] Kato, H.,J. Chem.Soc.Japan,58,605 (1937); Cf: Chem.Abstr.,31, 6581 (1937).
[4] Issa, I.M. ,Eid,S.A and Issa, R.M., Anal. Chim.Acta,11,275 (1954)
[5] Naidu,P.P. and Rao,G.G., Talanta, 18,112 (1971).
[6] Idem, Anal.Chem. 43, 281 (1971).
[7] Solymosi,F., Chemist-Analyst,52, 42 (1963).
[8] Van der Meulen, Chem.Weekblad, 31, 333 (1934); Cf: Chem. Abstr., 28 60799 (1934)Padma, D.K., Shaw, R.A., Vasudeva Murthy, A.R. and Woods ,M., Microchim. Acta, 849 (1974).
[9] Deshmukh, G.S and Bapat , M.G., Z. Analyst Chem., 156, 273 (1957)
[10] Bapat, M.G. and Tatwawadi , S.V., J.Sci. Research, Banaras Hindu Univ., 7, 235 (1957).
[11] Kaushik, R.L., Prasad , R., J.Ind.chem.Soc., 46, 923 (1969).
[12] Adams, D.F. and Gilbertson L.I.,Ind.Engng. Chem., Anal Edn., 14, 926 (1942).
[13] Colemen, W.C. and McCrosky, C.R., Ind. Engng.Chem. Anal Edn., 8, 196 (1936); 9, 431 (1937).
[14] Someya, K.,Z. anorg. Allgem. Chem., 187,357, (1930) Cf: Chem Abstr., 24; 23977 (1930).
[15] Muthmann, W. and Schafer, J. Ber., 26, 1008 (1893); Cf: Volumetric Analysis, Volume I I I, Kolthoff, I.M. and Belcher, R., Inetrscience publishers, NewYork,p. 327 (1957).
[16] Hirano,S.,J.Soc.Chem.Ind.Japan,41,266 (1938) Cf: Chem Abstr,32,89809(1938)
[17] Tarasova,V.A.,Ivonova,Z.I.,and Ignatenko,E.G.,Zavod Lab.Yugo-Vestoka SSSR,1,26(1972) Cf: Chem Abstr.80,78007d (1974)
[18] Sarin,R. and Pande, S.P., J.Inst. Chem. (India) 55,205(1983) 20. Lang,R.Z.,anorg.allgem.Chem.,142,280 (1925) Cf: Chem Abstr.,19,18307(1925)
[19] Singh,B. and Sood, K.C., Anal. Chim. Acta,11,317(1954) 22. Suseela, B.,Z.Anal.Chem.147,13(1955)
[20] Muraki,I.,J.Chem.Soc.Japan,PureChem.Sect.,76,198(1955) Cf: Chem Abstr., 49, 14567h(1955)
[21] Willard,H.H. and Fenwick, F.,J.Am. Chem. Soc.,45,933(1923)
[22] Tomicek,O.,Chem.Listy,32,442(1938) Cf: Chem Abstr.,33,28379,(1939)Syrokomskii,.V.S. and Knyazeva, R.N., Zavod.Lab.,15,1149(1949) Cf: Chem Abstr., 44,1357e (1950)
[23] Scherhaufer, A.M., Z.anal. Chem., 164, 327,(1958)

[24] Rao.V.R.S.,Curr.Sci.,39,83(1970) 29. Dikshitulu,L.S.A.,Raju,K.V. and Satyanarayana Dindi, Indian J.Chem.,15A,364 (1977)
[25] Ripan,R and Tautu ,G., Ser. Chem. 17, 59 (1972) Cf: Chem Abstr., 78, 105665j(1973)
[26] Sastry,G.S.,Acta.Cienc.Indiaca,Chem.,11, 171 (1985)
[27] Hubicki,H.,Sikorska,H.and Zychiewicz, Z.,Lublin polonia. Sect.AA.5,73(1950) Cf: Chem. Abstr., 27,9213h(1953)
[28] Tulyuppa,F.M.,Barkalov.V.S. and Usatenko,Y.I.,Khim.Tenkol (Khorkov) No.17.,166(1971) Cf: Chem Abstr., 76,67830h(1972)Selg,W.S. and Roberts, G.L., Microchem.J .,34, 140 (1986)
[29] Rao.B.V.,Kumar,J. and Rao.D. R. ,Ind. J.Chem., 21A. 1146(1982)
[30] Sushchinskii,A.D.,and Suprunovich, V.I., Vopr.Khim.Technol.,83,54 (1987) Cf: Chem. Abstr.,109,162442S (1988)
[31] Pagel,H.A. and Miers ,J.C., Ind. Engng. hem.,Anal.End.,10,334,(1938) .