CHAPTER - IIB

METHYL THIENYLKETONE THIOSEMICARBAZONE AS A SPECTROPHOTOMETRIC REAGENT FOR RUTHENIUM (III)

Introduction :

Ruthenium is one of the noble elements. Its common oxidation states are II, III and IV. It finds wide applications as a catalyst in organic synthesis. It is also used as a hardening agent to platinum and palladium used in electrical contacts and jewellery. Complex ruthenium alloys with and without added as osmium are very hard and used for pen tips, nonmagnetic instruments, pivotes and similar items. It is required in pure state many times.

Beamish[1] has reviewed the reagents used upto 1965 for the spectrophotometric determination of ruthenium. Thiourea[2] is the common reagent used for routine analysis of ruthemium in an alcoholic acid medium. In this method the intemsity of the colour depends markedly upon the acid concentration, time of heating and the temperature. Besides the interferences from base matels and other platinum metals, the sensitivity of the method is low. Several modified procedures have been developed. Among the various chromatographic reagents reported for the colorimetric estimations of ruthenium, the most important are substituted thiosemicarbazides [3-4], phenanthroline [5,6], oxine[7],

diphenyl thiourea[4], dithio oximide[8], naphthols[9,10], tropbone[11], oximes [12,13,14], 3-nitroso-pyridine-2,6-diol[15], diphenyl thiovioluric acid[16], 3-nitroso-4-hydroxy-5,6-benzocumarin[17], prochlorperazine maleate[18], diethazine. hydrochloride[19], ethyl iso-nitroso-aceto acetate[20], Promethazine hydrochloride[21], trifluoperazine dihydrochloride[22], acetothio acetanilide[23], mepazine hydrochloride[24], Xylenol orange[25], TAR[26], PAR[27] and arsenazo[28], etc.

Although the series of organic azine compounds reported by Sanke Gowada et al. for photometric determination of Ru(III) in aqueous acid media are sensitive, there is a interference of Pd(II) Os(VIII) Au(III) V(V) and Ce(IV). The complexes have the absorption maxima around 515 to 530 nm.

Shome et al. developed the methods for photometric determination of ruthenium (III) using various organic thiohydrazides [29,30,31]. The reagents are highly sensitive but lack selectivity and requires longer time of heating for full colour development.

Oximidobenzotetronic acid [32] is useful over wide pH range 1-12, but its sensitivity is very poor besides interferences from many metals.

The heating of the aqueous phase is necessary for attaining full colour intensity of the ruthenium complex in case of reagents e.g. Xylenol orange, (70 min.), 3-nitroso pyridine-2-6-diol (60 min) 4,5 diamino-6-hydroxy pyrimidinium sulphate[33] (75 min.)

3-nitroso-4-hydroxy-5,6-benzocoumarin (40 min), ferrozine[34] (3 hrs.),4,5-diamino-2-mercaptopyrimidin-6-ol (45 min).

The reagents which suffer from large number of interferences of both base metals and platinum metals include nitroso-R-salt[35], diphenyl thiovioluric acid, 4,5-diamino-6-hydroxy pyrimidinium sulphate, 3-nitroso-4-hydroxy-5,6-benzocoumarin, glycine[36], β-dithionaphthalic acid[37], arsenazo-I and ferrozine.

Methods of determination of ruthenium (III) using, 2-mercapto-benzimidazole[38], thiocynate [39], furil-α-monoxime, 1-naphthylamino-3,5,7 - trisulphonic acid[40] lack sensitivity.

However, the present method is free from the disadvantages mentioned for the above methods. The method is highly selective, simple and reproducible. MTKT reacts with ruthenium(III) in hot aqueous acidic medium to form green complex, which is measured at 600 nm. against the reagent blank.

Experimental

Standard Ruthenium (III) Solution

Standard Ruthenium (III) was prepared by dissolving 1 g. ruthenium (III) chloride hydrate (M/S Johnson Matthey, London) in dilute AR hydrochloric acid (1M) and diluting to 1000 ml with distilled water and then standarised[1] . Working solutions of lower concentrations were made from it by diluting the stock solution with distilled water as required.

Reagent Solution :

0.25 % W/V solution of MTKT was prepared in methanol.

Standard solutions of diverse ions were prepared by dissolving AR grade reagents in distilled water or dilute hydrochloric acid. All the organic solvents were used after double distillation. The mineral acids, used to adjust the acidity of the medium were of AR grade.

Apparatus :

All absorbance measurements were carried out with a specol (Carlzeiss Jena made in Germany DDR) equipped with 1 Cm.glass or quartz cells.

Recommended Procedure :

To an aliquot of the solution containing 400 µg. of ruthenium, enough hydrochloric acid was added so as to make it 6.5 M in a final volume of 25 ml followed by the addition of 4 ml methanol and 10 ml of the reagent solution. This solution was heated for 35 min on boiling water bath, cooled and then quantitatively transferred to 25 ml volumetric flask. It was made up to volume with double distilled water. The optical density of ruthenium (III) complex was measured against reagent blank prepared in the same manner excluding ruthenium at 600 nm.

Results And Discussion :

Spectral Characterstics :

Fig. 1.1 shows the absorption spectrum of ruthenium (III)-

MTKT Complex containing 2.37 x 10^{-4} M ruthenium and 2.5 x 10^{-3} M of reagent using the reagent blank. Absorption measurements were made in spectral range 420 to 730 nm. From fig 1.1 it is observed that the complex has two absorption maxima, one at 450 nm and other at 600 nm, the wevelength 600 nm is suitable to ruthenium determination, at which the molar extinction coefficient is 2357 L $mole^{-1}$ cm^{-1}.

Effect of Time on Absorbance:

In order to study effect of time on absorbance of ruthenium(III)-MTKT complex containing 1.58 x 10^{-4} M ruthenium at 6.5 M acidity, absorption measurements were recorded at different time intervals, at 600 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant over a period of 6 hours. Hence, the time of absorbance measurement is not crifical.

Effect of Reagent Concentration :

Solution containing 1.58 x 10^{-4} M ruthenium (III) but different amounts of reagent varying from 0.5 to 12 ml. of 1.25 x 10^{-2} M reagent solution were used. Acidity of the solution was adjusted to 6.5 M with hydrochloric acid and heated for 35 min.After cooling, the solution was made up to 25 ml with double distilled water. Absorbance measurements were recorded at 600 nm against simultenously prepared reagent blank. From Fig 1.3 it is seen that 1.58 x 10^{-4} M ruthenium (III) solution

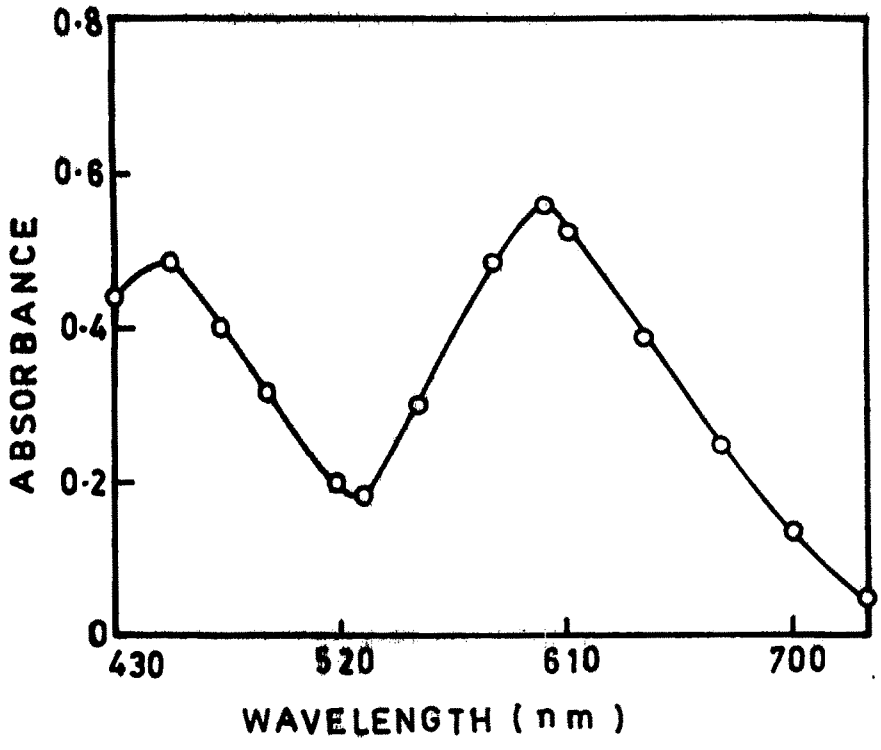
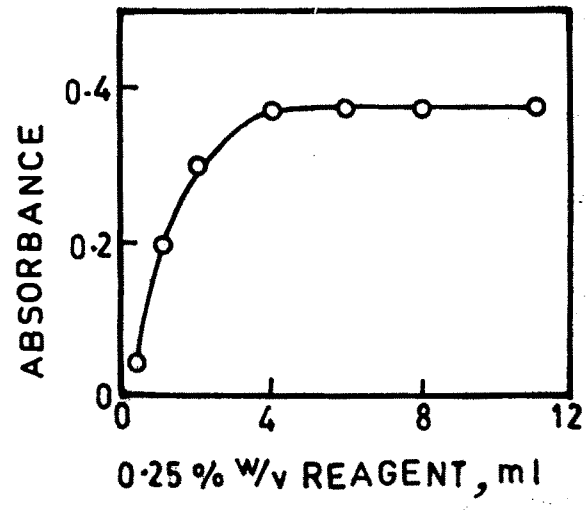


Fig. 2·2 — SPECTRUM OF Ru(III)–MTKT COMPLEX. Ru(III), 24 ppm

Fig. 2·3 — EFFECT OF REAGENT CONCENTRATION. Ru(III), 16 ppm.



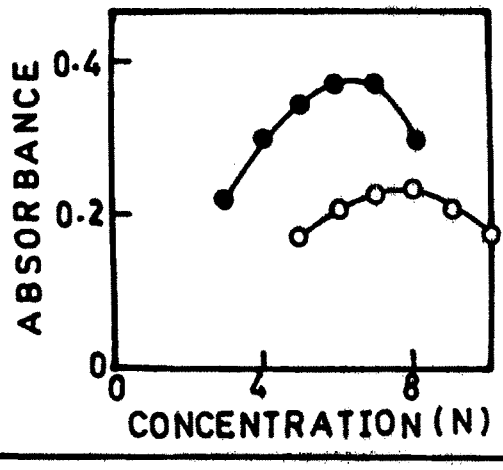


Fig. 2·4 — EFFECT OF ACID CONCENTRATION. Ru(III), 16 ppm.

—●— HCl

—○— H_2SO_4

required minimum 2.0 x 10^{-3} M reagent solution for maximum colour development. However , 5 x 10^{-3} M reagent solution was used for further studies to ensure maximum colour intensity of ruthenium complex.

Effect of Acid concentration :

A series of solutions containing 1.58 x 10^{-3} M ruthenium and 5.0 x 10^{-3} M reagent solution but varying in acidity from 1 to 9 N were prepared and the absorbance measurement were recorded at 600 nm.Results of studies are summerised in table No.2.1.

It was observed from fig. 2.4 that no change in absorbance took place over the acidity range of hydrochloric acid 6-7 M and of sulphuric acid at 8 N sharp. Molar extinction coefficient of hydrochloric acid system is more than sulphuric acid system. Hence, concentration of hydrochloric acid was maintained at 6.5 M in further studies.

Table 2.1 Effect of Acidity

Ru(III) = 1.58×10^{-3} M [MTKT] = 5.0×10^{-3}M

Sr. No.	Normality of acid	Absorbance at 600nm	
		For hydrochloric acid	For sulphuric acid
1	2	-	-
2	3	0.255	-
3	4	0.300	-
4	5	0.350	0.175
5	6	0.375	0.225
6	7	0.375	0.260
7	8	0.305	0.275
8	9	0.280	0.225

Effect of Time of heating:

Heating of the aqueous phase in a boiling water-bath necessary for full colour development was studied by varying the time of heating in intervals of 5,10,15,20,25,30,35,40,45, 50,55 and 60 min. Results were plotted in fig 1.5 indicated that, the heating of the aqueous phase for 30 min was enough for complete complexation. But there is no effect of heating on the complex upto 50 min. Heating the aqueous phase for 35 min.was recommended for studies.

Validity of Beer's law And Sensitivity :

The solutions containing ruthenium (III) in the concentration range upto 48 ppm were used for the study of Beer's law. The colour of the complex was developed as described in general procedure using 10 ml of 1.25×10^{-2} M reagent, and measured at 600 nm against simultaneously prepared reagent blank. The absorbance was plotted against the ppm of ruthenium (III) taken Fig. 1.6. The curve indicates that, there is a rectilinear relationship between the absorbance and the concentration of ruthenium (III) in the range 4-32 ppm. The Sandell sensitivity[42] of the reaction as calculated from Beer's plot is found to be 43 ng Ru (III) cm^{-2} at 600 nm for log $I_o/I = 0.001$. The Ringbom's[43] plot (Fig 1.7) indicates the optimum concentrations range for determination of Ru (III) complex to be 8 to 32 ppm.

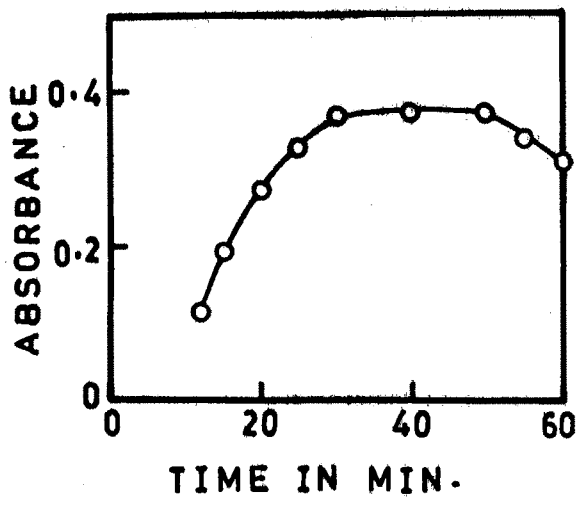
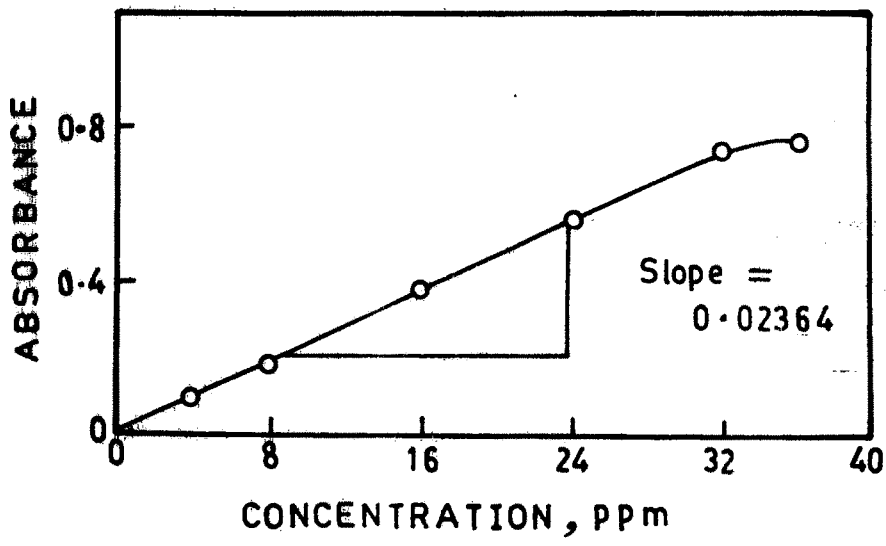


Fig. 2·5 —
EFFECT OF HEATING
Ru(III), 16 ppm.

Fig. 2·6 —
VALIDITY OF
BEER'S LAW
Ru (III)



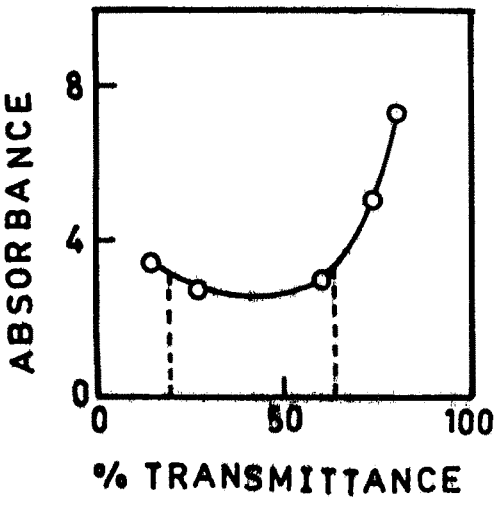


Fig. 2·7 —
RING BOUM PLOT.

Reproducibility, Accuracy And Precision :

For study of reproducibility and accuracy of the method, absorbance measurements with 10 different identical solutions containing 24 ppm ruthenium (III) each, were performed as per recommended procedure and concentrations was determined by using calibration curve. The results are shown in table 2·2 and 2·3.

Average of these ten readings was calculated and deviation from the average reading was found out in each case and then standard deviation was calculated. From the standard deviation reproducibility of the results with 95 % confidence limit was calculated. Also the Sandell's sensitivity was calculated from Beer's law graph.

Standard deviation

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=n} (Xi-\bar{X})^2}{n}}$$

$$= \sqrt{\frac{0.072}{10}}$$

$$= 0.089$$

Reproducibility with 95% confidence limit

$$= \bar{X} \pm 2.26 \times \frac{\sigma}{\sqrt{n}}$$

$$= 24.033 \pm 2.26 \times \frac{0.089}{\sqrt{10}}$$

$$= 24.033 \pm 0.064$$

Error = observed reading - Actual reading

$$E = 24.033 - 24.000$$

$$= 0.033$$

% Realative error (Accuracy)

$$= \frac{E \times 100}{10} =$$

= 0.33 %

Molar Extinction coefficient =

a) $\epsilon = \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{At. wt.}$

$= \frac{0.375}{16} \times 1000 \times 101$

$= 2368$

b) $\epsilon_{graph} = \text{slope} \times 1000 \times 101$

$= 0.02464 \times 1000 \times 101$

$= 2388$

Sandell's Sensitivity = - (S)

$= 10^3 \times \text{At Wt.} \times \text{min}$

where $\text{min} = \frac{D \text{ min}}{x \text{ b}}$

$= 10^3 \times 101 \times \frac{0.001}{2368 \times 1}$

$= 42.6 \text{ ng cm}^{-2}$

% Coefficient of variation =

$\text{c.v.} = \frac{6 \times 100}{\bar{X}}$

$= \frac{0.004 \times 100}{0.085}$

$= 4.707$

Table 1.2 Precision and Accuracy of the Method

Amount of Ru(III) = 24 ppm, [MTKT] = 5.00×10^{-3}M

Sr. No.	Absorbance observed	ppm of Ru(III) found , X	$X - \bar{X}$	$(X - \bar{X})^2$
1	0.565	24.09	0.057	0.0033
2	0.560	24.00	- 0.033	0.0011
3	0.555	23.90	- 0.133	0.0177
4	0.560	24.00	- 0.033	0.0011
5	0.570	24.18	0.147	0.0216
6	0.555	23.90	- 0.133	0.0177
7	0.565	24.09	0.057	0.0033
8	0.560	24.00	-.0.033	0.0011
9	0.565	24.09	0.057	0.0033
10	0.565	24.08	0.047	0.0022
		240·33		0·0724

$$\bar{x} = \frac{240 \cdot 33}{10}$$

$$= 24 \cdot 033$$

Table - 2.3, % Coefficient of Variation.

$[MTKT] = 5.0 \times 10^{-3}$ M

Sr. No.	Concentration µg/25 ml.	Mean Absorbance	Standard deviation	% Coefficient of variation
1	100	0.085	0.0040	4.707
2	200	0.180	0.0042	2.333
3	400	0.375	0.0040	1.0670
4	600	0.565	0.0038	0.6726
5	800	0.740	0.0040	0.5404

Effect of Diverse Ions :

The effect of diverse ions was studied using 0.4 mg ruthenium (III) and 5.0×10^{-3} M reagent in final volume of 25 ml at 6.5 M acidity. An error of less than 2 % in absorbance was considered to be tolerable. The tolerance for the various foreign ions tested is shown in table 2.4. Table showes that the only cation showing the interference in the determination of ruthenium (III) was cadmium (II). There was no interference from 5 mg each of tin (II), molybdenum (VI), barium (II), calcium (II), strontium (II), iron (II), Rhodium (III), Tellurium (IV), Selenium (IV), 2 mg each of vanadium (V), iron (III), Cobalt (II), Iridium (III), Palladium (II), 1 mg each of zinc (II), mercury (II), Nickel (II), Copper (II), Osmium (VIII), chromium (VI). The method could also tolerate fairly large amount of EDTA, acetate, citrate, oxalate, tartarate, iodide, phosphate and ascorbate. The anions like thiourea, thiosulphate, thiocyanate interfere severely in ruthenium (III) determination.

Table 2.4 Effect of diverse ions

Ru (III) taken 0.4 mg; [MTKT] = 5×10^{-3}M
Acidity = 6.5 M HCl λmax = 600 nm

Foreign ions.	Amount tolerated, mg	Foreign ions	Amount tolerated, mg
Zn(II)	1.00	Ca(II)	5.00
Cd(II)	none	Sr(II)	5.00
Hg(II)	1.00	Pd(II)	2.00
Sn(II)	5.00	Cr(VI)	1.00
V(V)	2.00	Se(IV)	5.00
Mo(VI)	5.00	EDTA	40.00
Fe(II)	5.00	Thiourea	none
Fe(III)	2.00	Acetate	60.00
Co(II)	2.00	Citrate	40.00
Ni(II)	1.00	Oxalate	25.00
Cu(II)	1.00	Tartarate	40.00
Mn(II)	10.00	Thiosulphate	none
W (VI)	10.00	Thiocyanate	none
Ba(II)	5.00	Iodide	50.00
Pt(IV)	10.00	Phosphate	50.00
Rh(III)	5.00	Ascorbate	50.00
Ir(III)	2.00		
Os(VIII)	1.00		
Au(III)	1.00		
Te(IV)	5.00		

References :

1 Beamish, F.E. "Analytical chemistry of the nobel metals," Pergamon Oxford, 1966.

2 Ayres, G.H. and Young, F.
Anal, Chem. 22 (1950) 1277.

3 Geilmann, W. and R.Neeb,
Z.Anal. Chem. 152 (1956) 96.

4 Kaight, S.B.,Parks, R.L., Leidt, S.C. and Parks, K.L.
Anal. Chem. 29 (1957) 1442.

5 Banks, C.V. and O' Laughlin, J.W.
Anal. Chem. 29 (1957) 1412.

6 Vita,O.A. and Tririsonno, C.F.
NGCL Applic. 1 (1968) 739.

7 Toyoaki Kato
Bull,Chem.Soc.Japan 37 (1964) 1453.

8 Jacabs, W.D., and Yoe,J.H.
Talanta 2 (1959) 270

9 Manning, D.L. and Mannis, O.
Anal. Chem. 34 (1962) 94.

10 Kesser, G., Meyer, R.J. and Larsen, R.P.
Analy. Chim. Acta, 36 (1966) 221.

11 Rizvi, G.H., Gupta, B.R.and Singh, R.P.
Anal. Chim. Acta 54 (1971) 295

12 Sindhwani, S.K. and Singh R.P.

Anal, Chim.Acta 55 (1971) 409

13 Manku, G.S.,

Curr.Sci. 45 (1976) 256

14 Savostia, V.M., Shpigun, O.A., Klimova, Kolotyrkina, I. Ya and Peshkova, V.M. Zh.Anal. Khim.34 (1979) 607

15 Mc Donald, C.W. and Bedenbaugh, J.H. Mikrochim. Acta, 3 (1970) 612.

16 Chawala, R.S., Sangh, R.P. and Trikha, K.L.

Talanta, 18 (1971) 1245

17 Kohli, N. and Singh, R.P.

Talanta, 21 (1974) 638

18 Gowda, H.S. and Ramappa, P.G.

Anal. Chim. Acta, 83 (1976) 283

19 Gowda, H.S. and Ramappa, P.G.

Talanta, 23 (1976) 252

20 Patil, M.R. and Haldar, B.C.

Talanta, 23 (1976) 550

21 Gowda, H.S. and Keshvan, S.

I.J. Chem. Sect A, 14 (1976) 630

22 Gowda, H.S. and Ramappa P.G.

I.J. Chem Sect. A 14 (1976) 631.

23 Datta, K. and Das, J.

I.J.Chem. Sect. A 14 (1976) 917

24 Gowda, H.S. and Keshvana, B.

I.J.Chem. Soc. 54 (1977) 603

25 Shrivastava, S.C. and Day, A.K. Chim. Analyt,
51 (1969) 131

26 Ivanova, V.M., Busev, A.I., Popova, L.V.
and Bogdanovich, L.I.
Zh. analit. Khim 24 (1969) 1064.

27 Boganovich, L.I., Busev, A.I. and Ivanov, V.M.
Vest mosk, gos. Univ. Ser, Khim. 12 (1971) 197

28 Khalifa, H. and Issa, Y.M.
Z. anal. Chem. 274 (1975) 126

29 Shome, S.C. and Gangopadhyay, P.K.
Anal. Chim. Acta 65 (1976) 603

30 Shome, S.C., Gangopadhyay, P.K., and Gangopadhyay, S.
Talanta, 23 (1976) 603

31 Shome, S.C. Nandy, S. Guhathakurta, A., Ghosh
N.C., Das, H.R. and Gangopadhyay, P.K.
Mikrochim. Acta (Wein) 1978 (II) 343

32 Manku, G.S., Bhat, A.N. and Jain, B.P.
Talanta, 14 (1967) 1229

33 Veer, C.G., Raghu, Rhodes, Thornton and Mc Donald, C.W.
Microkhim Acta 4 (1974) 611

34 Kundra, S.K., Katyal, M. and Singh, R.P.
Curr. Sci. 44 (1975) 548

35 Millar, D.J., Shrivastav, S.C. and Good, M.L.
Anal. Chem. 37 (1968) 739

36 Bukanova, A.E., Prokof Wa, I. V. and sidoveva, J.P.
Z . analt. Khim 29 (1974) 2109

37 Gorniak, H.

Z. analyt. Chem 275 (1975) 205

38 Lomakina, L.M., Ignat eva, T.L. and Busev, A.I.

Zh. Anal. Khim , 33 (1978) 527

39 Marczenko, Z. and Balcekzak, M.

Anal. Chim. Acta, 109 (1979) 123

40 Steele, E.L. and Yoe, J.H.

Anal Chim. Acta , 20 (1959) 211.