

## **CHAPTER –II**



# **Experimental Technique**

The kinetics and mechanism of oxidation of benzoic acid hydrazide by potassium bromate catalyzed by Anderson type sodium hexamolybdochromate(III) and octamolybdomanganate(II) has been studied under pseudo-first-order condition by keeping excess hydrazide over that of oxidant in aqueous acidic medium. The experimental results obtained include:

1. Effect of variation of reactants concentration on the rate of reaction and determination of order of the reaction with respect to each reactant.
2. Effect of catalyst concentration on the rate of reaction and determination of order with respect to it.
3. Effect of variation of hydrogen ion concentration.
4. Effect of temperature variation and to evaluate thermodynamic parameters for the reaction.
5. Product analysis for stoichiometry determination.
6. Effect of ionic strength, solvent polarity and acrylonitrile.

#### **Preparation and standardization of solutions:**

The doubly distilled water was used throughout the work. The entire chemicals used for experiments were of reagent grade. The  $\text{KBrO}_3$  (BDH) solution was prepared by dissolving it in water and standardized iodometrically. The benzoic Acid hydrazide was prepared by esterification of the corresponding acids in ethanol followed by their conversion to hydrazide according to the reported method[1] and its solution was prepared by dissolving in water. Ionic strength was maintained using KCl, and to vary hydrogen ion concentration HCl (BDH) was used. The double distilled water was used for preparation of stock solutions. The stock solutions were stored in airtight amber colored bottles and kept in the dark.

The  $0.1 \text{ mol dm}^{-3}$  stock solution of Benzoic acid hydrazide and  $0.01 \text{ mol dm}^{-3}$  solution of Potassium bromate were prepared by dissolving appropriate amounts of them in double distilled water.

The solutions of catalysts sodium hexamolybdochromate(III) and octamolybdomanganate(II) and  $1.0 \text{ mol dm}^{-3}$  of hydrochloric acid were prepared by dissolving them in double distilled water. The stock solution of  $0.1 \text{ mol dm}^{-3}$

sodium thiosulphate was prepared by dissolving a calculated quantity of it in double distilled water and standardized[2] iodometrically against  $\text{KBrO}_3$  using starch indicator. The stock solution was diluted to the required concentration & then used. The solutions of  $2 \text{ mol dm}^{-3}$  sulphuric acid and 5% KI were prepared everyday by dissolving calculated amount of it in double distilled water. Starch solution was prepared by dissolving it in boiling water and little  $\text{CCl}_4$  was added to it.

The stock solutions used were of the following concentrations.

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1.	Benzoic acid hydrazide solution	$0.1 \text{ mol dm}^{-3}$
2.	Potassium bromate solution	$0.01 \text{ mol dm}^{-3}$
3.	Sodium hexamolybdochromate(III)	$0.001 \text{ mol dm}^{-3}$
4.	Octamolybdomanganate(II)	$0.001 \text{ mol dm}^{-3}$
5.	Hydrochloric acid	$1.0 \text{ mol dm}^{-3}$
6.	Sodium thiosulphate solution	$0.1 \text{ mol dm}^{-3}$
7.	Potassium iodide	5 %
8.	Sulphuric acid	$2.0 \text{ mol dm}^{-3}$
9.	Potassium chloride	$1.0 \text{ mol dm}^{-3}$
10.	Starch indicator	freshly prepared everyday

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#### Method of following Kinetics:

The main features of the experimental method used to follow the kinetics of oxidation of benzoic acid hydrazide by potassium bromate catalyzed by Anderson type sodium hexamolybdochromate and octamolybdomanganate(II) are as follows:

- 1) Throughout experimental work standard Pyrex glassware were used.
- 2) The reaction mixture was placed in thermostated water bath & its temperature maintained constant. ( $\pm 0.1^\circ\text{C}$ )
- 3) The reactions were carried out in a stoppered conical flask (100 ml).
- 4) The reactions were carried out under pseudo first order conditions keeping concentration of hydrazide excess to that of potassium bromate.

- 5) Flask 1 – The calculated quantities of standard solution of benzoic acid hydrazide, sodium hexamolybdochromate(III) and hydrochloric acid.
- 6) Flask 2 – The calculated quantities of potassium bromate and hydrochloric acid.
- 7) The conical flasks were thermostated for 30 minutes.
- 8) The reaction was initiated by adding the thermostated solution from flask 2 to flask 1. The time of initiation of reaction i.e. time of mixing of the solutions was recorded as zero time.
- 9) After mixing immediately 5 ml of this reaction, mixture was transferred to conical flask containing 5 ml of 5% KI & 5 ml of 2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The solution was titrated against Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using starch as indicator. Then at definite time intervals, 5 ml of this reaction mixture were titrated adopting same procedure.
- 10) The reactions were usually followed up to 90% completion.

The pseudo-first-order rate constants were determined from pseudo-first - order plots of log [oxidants] against time. The pseudo-first -order plots were linear for more than 70% completion of reaction and rate constants were reproducible within 6%. The example runs are shown in Table 2.1 and Table 2.2 for sodium hexamolybdochromate(III) and octamolybdomanganate(II) catalyzed reactions respectively. The corresponding pseudo first-order plots are shown in figure 2.1 and 2.2.

**Table 2.1**

Oxidation of benzoic acid hydrazide by bromate catalyzed by Anderson type hexamolybdochromate (III) in aqueous acidic medium at 25<sup>o</sup> C.

Example Run

$$10^2 [\text{hydrazide}] = 1.0 \text{ mol dm}^{-3}$$

$$10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$$

$$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$$

$$10^4 [\text{H}_6\text{Cr}^{\text{III}} \text{Mo}_6\text{O}_{24}]^{3-} = 1.0 \text{ mol dm}^{-3}$$

$$I = 0.5 \text{ mol dm}^{-3}$$

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Time min	Burette Reading ml	-log [ KBrO <sub>3</sub> ]
0	30.0	2.23
5	23.2	2.33
10	16.8	2.47
15	11.6	2.64
20	7.0	2.86
25	4.6	3.04
30	3.4	3.17
35	2.3	3.34

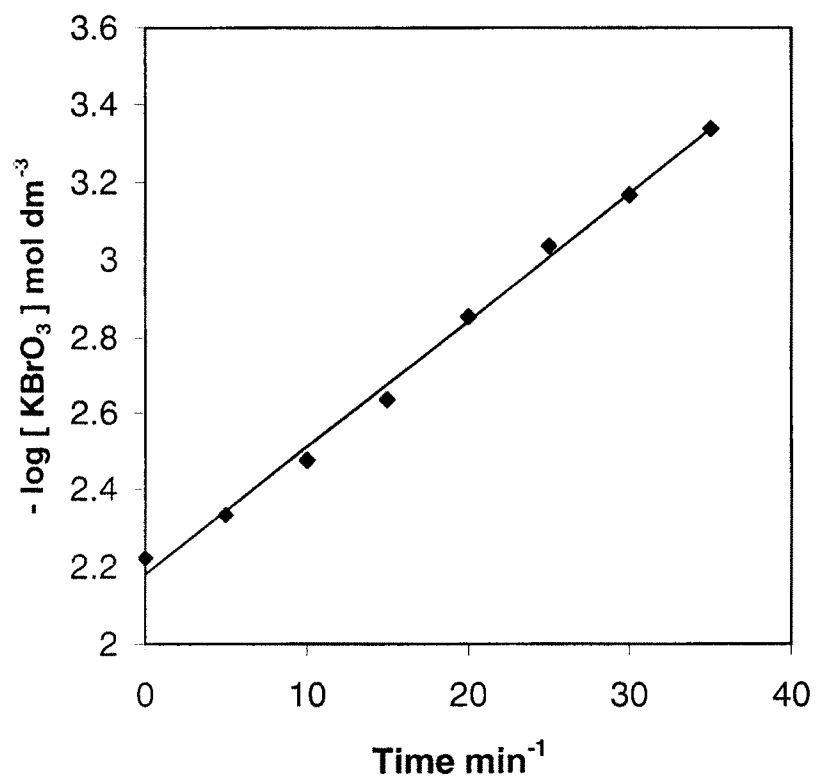
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**Figure 2.1**

Oxidation of benzoic acid hydrazide by bromate catalyzed by Anderson type hexamolybdochromate( III ) in aqueous acidic medium at 25<sup>0</sup> C.

Example Run

Conditions as in Table 2.1



**Table 2.2**

Oxidation of benzoic acid hydrazide by bromate catalyzed by octamolybdomanganate(II) in aqueous acidic medium at 27<sup>0</sup> C.

Example Run

$$10^2 [\text{hydrazide}] = 1.0 \text{ mol dm}^{-3}$$

$$10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$$

$$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$$

$$10^4 [\text{Mn}^{\text{II}}\text{Mo}_8\text{O}_{27}]^{4-} = 1.0 \text{ mol dm}^{-3}$$

$$I = 0.5 \text{ mol dm}^{-3}$$

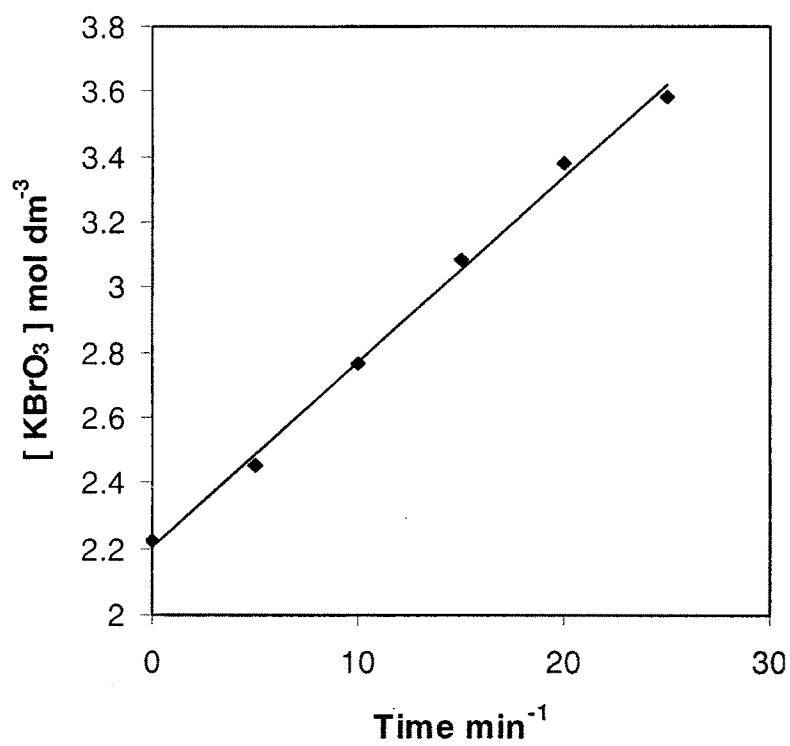
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Time min	Burette Reading ml	-log [ KBrO <sub>3</sub> ]
0	30.0	2.23
5	17.6	2.45
10	8.6	2.76
15	4.1	3.09
20	2.1	3.38
25	1.3	3.59

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**Figure 2.2**

Oxidation of benzoic acid hydrazide by bromate catalyzed by octamolybdomanganate(II) in aqueous acidic medium at 27<sup>0</sup> C.  
Condition as in Table 2.2





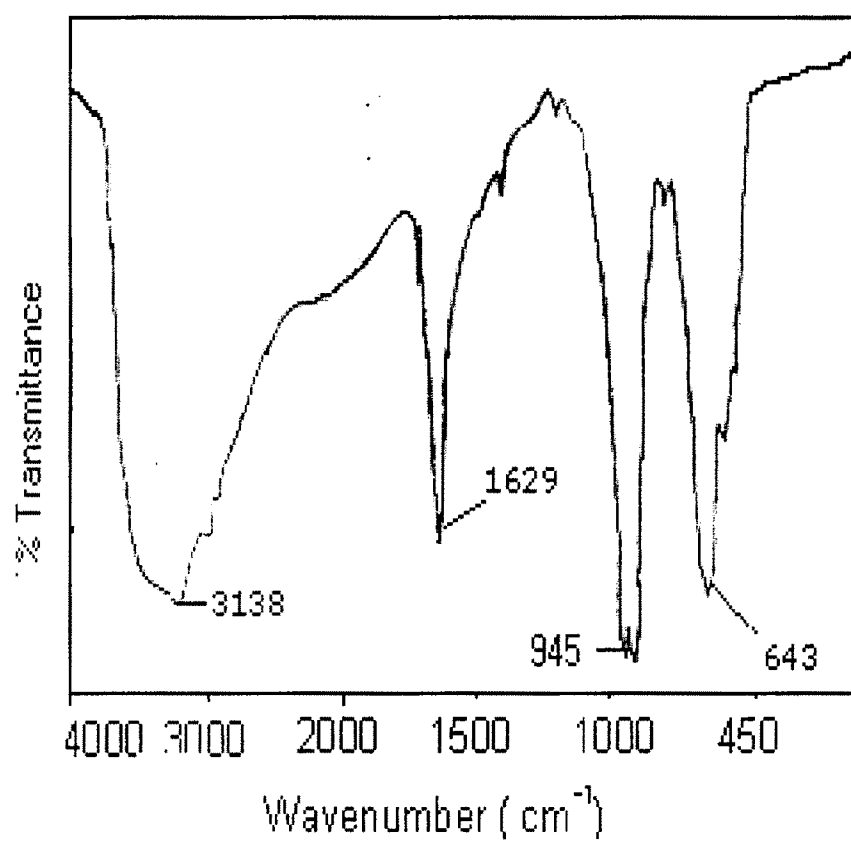
### **Preparation and characterization of Sodium hexamolybdochromate (III):**

The catalyst Sodium hexamolybdochromate (III) was prepared by the previously reported method [3]. The pH of a solution containing 14.5 g of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 30 ml of water was adjusted to 4.5 with concentrated  $\text{HNO}_3$ . A second solution was made by dissolving 4.0 g of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 5 ml of water. Both the solutions were mixed together, and the mixture was boiled for 1 min and filtered while hot. The filtrate was set aside for crystallization and crystals started to appear in 1 hr. The solution was allowed to stand for 2 weeks before the precipitate was filtered off and washed several times with cold water. Reddish purple crystals were obtained.

The complex  $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6] \cdot 8\text{H}_2\text{O}$  was studied by AAS analysis. 100 mg of recrystallized sample was dissolved in doubly glass-distilled water. 5 ml of this stock solution was diluted to 100 ml and used for AAS analysis of Cr and Mo metals using Perkin-Elmer AAnalyst-300. The complex  $\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6] \cdot 8\text{H}_2\text{O}$  shows (Theoretical): Na- 5.6303 % (5.6052 %), Cr- 4.2227 % (4.2242 %) and Mo-46.217 % (46.2109 %).

The FT-IR spectrum of sodium hexamolybdochromate(III) was recorded on Perkin-Elmer-783 instrument in KBr is shown in figure 2.3. The FT-IR spectrum shows the peaks at  $945\text{ cm}^{-1}$ ,  $915\text{ cm}^{-1}$  and  $643\text{ cm}^{-1}$  corresponding to  $\text{Mo-O}_d$ ,  $\text{Mo-O}_b$ -Mo,  $\text{Mo-O}_c$ -Mo stretching motion of Anderson structure. The broad peak centered at  $3138\text{ cm}^{-1}$  and sharp peak at  $1629\text{ cm}^{-1}$  indicates water associates with Anderson structure as either in lattice or in the co-ordinated form.

Figure 2.3 :The FT-IR spectrum of Sodium hexamolybdochromate (III).



### **Preparation and characterization of octamolybdomanganate(II):**

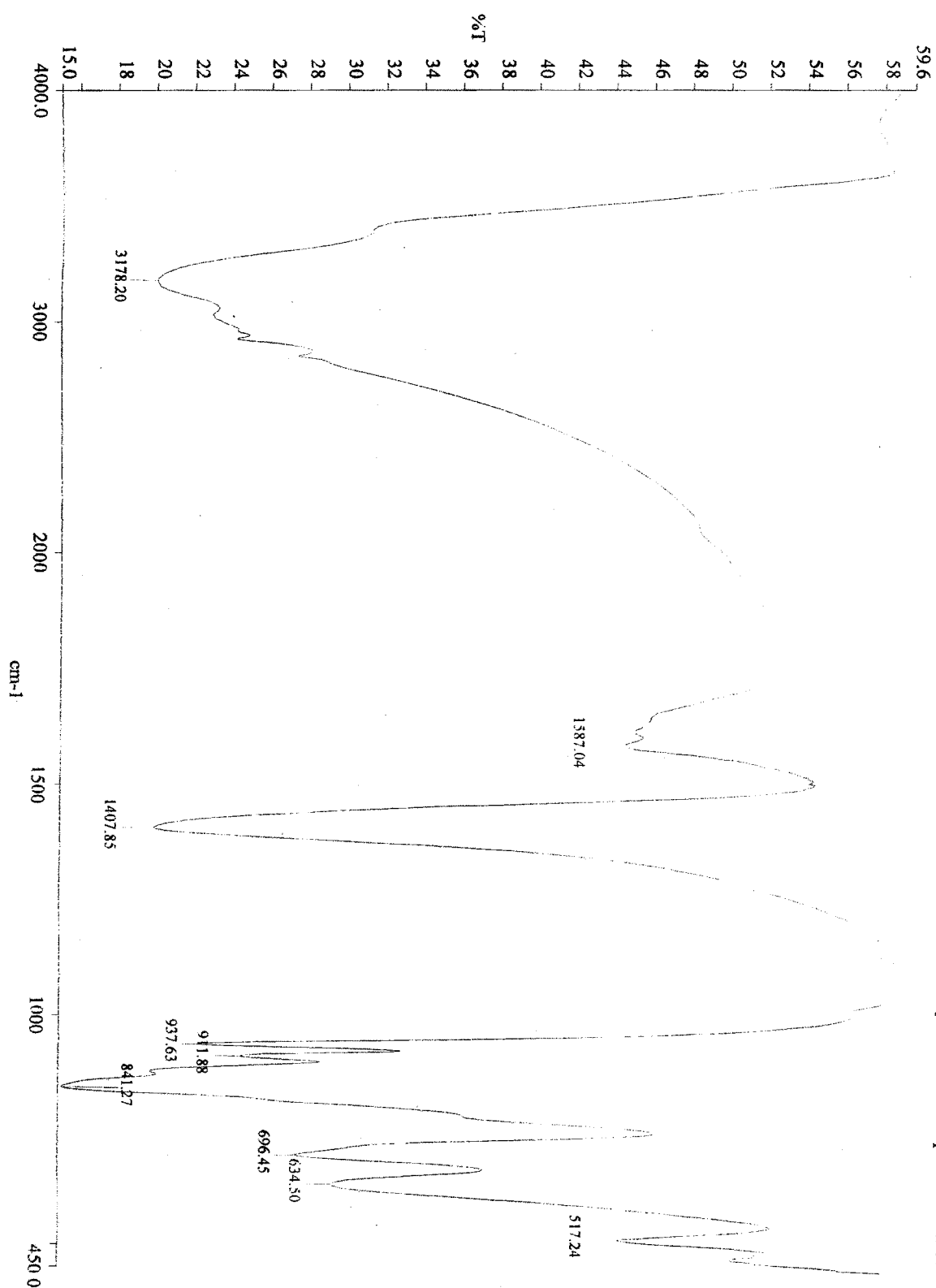
The catalyst octamolybdomanganate(II) was prepared by the previously reported method as follows; 2.3661 gm ( 14 m mol ) of manganese(II) sulphate monohydrate ( S. D. Fine ) was dissolved in 100 ml of water and slowly added to a solution of ammonium heptamolybdate tetrahydrate ( 22.2462 gm 100 ml of water ) ( S. D.Fine ) at 40<sup>0</sup>C with constant stirring. After mixing, the light- yellow solution was cooled to 5<sup>0</sup>C overnight. The light-yellow colored crystals were collected by decantation after three days. These crystals were recrystallised thrice from hot water.

The complex  $(\text{NH}_4)_4[\text{MnMo}_8\text{O}_{27}] \cdot 20\text{H}_2\text{O}$  was analyzed by AAS of Mn and Mo metals using Perkin-Elmer AAnalyst-300.

The complex  $(\text{NH}_4)_4[\text{MnMo}_8\text{O}_{27}] \cdot 20\text{H}_2\text{O}$  shows (Theoretical): Mn- 3.7 % (3.2%), and Mo-49.78 % (45.55 %).

The FT-IR spectrum of octamolybdomanganate(II) was recorded on Perkin-Elmer-783 instrument in KBr is shown in figure 2.4. The FT-IR spectrum shows the peaks at 938  $\text{cm}^{-1}$ , 912  $\text{cm}^{-1}$  and 841  $\text{cm}^{-1}$  corresponding to Mo-O, Mn-O stretching and at 696  $\text{cm}^{-1}$ , 635  $\text{cm}^{-1}$ , 517  $\text{cm}^{-1}$  due to Mo-O-Mo and Mo-O-Mn stretching motion. The broad peak centered at 3178  $\text{cm}^{-1}$  and sharp peak at 1587  $\text{cm}^{-1}$  indicates water associates with structure lattice.

Figure 2.4 : FT-IR spectrum of octamolybdomanganate(II)



Description:

Spectrum Name: SDK Mn(II) COMPLEX.002

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C.F.C. Shivaji Uni. Kolhapur Date: 1/30/02

**References:**

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2. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis' 3<sup>rd</sup> ed. (1961) 319.
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4. S. J. Dunne, J, A. Irwin, R. C. Burns, G. A. Lawrance and D. C. Craig, J.Chem.Soc.Dalton Trans.(1993) 2717.