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### **Valency stabilization of Polyvalent Iron Ions in Solution By some Organic additives during Gamma Irradiation**

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#### **ABSTRACT**

Valency stabilization of polyvalent ions in gamma irradiated aqueous solutions is sometimes necessary for the success of some chemical operations. In some previous publications valency stabilization of some polyvalent ions in solution upon gamma irradiation was achieved by using additives capable of interacting with the oxidizing or reducing species formed by water radiolysis in the medium. The results showed that the duration of valency stabilization depends on the concentration of the additives used.

In the present work, a series of some organic additives has been used to investigate their capability in inducing valency stabilization of polyvalent iron ions when subjected to extended gamma irradiation periods. The results showed that the efficiency of valency stabilization depends on the amount and chemical structure of the organic additive used

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#### **INTRODUCTION**

Protective effects against structural and ionic changes induced by traces of some chemicals during irradiation by X- or  $\gamma$ - radiations have been known since a long time. It was suggested that protection in radiolytic systems is a phenomenon that is greatly related to competitive reactions. Competition depends on the reaction rates and also on the equilibrium constant of the oxidation reduction reactions occurring in the polyvalent ions aqueous systems.

The protective effect of additives was observed long ago by Fricks et al.<sup>(1)</sup> in aqueous acetic acid solutions irradiated by X-rays. The addition of formic acid highly reduced the oxidation of acetic acid even if the concentration of the protective agent is in 100 times lower than the concentration of acetic acid.

Other authors reported on the existence of a protective effect on the decolorization of methylene blue by  $\alpha$  rays, in presence of formic, malonic acids or gelatin<sup>(2)</sup>. Saturated Compounds such as formaldehyde, ethyl alcohol, and galactose, act more weakly than unsaturated Compounds<sup>(3)</sup>.

Many studies have been carried out to investigate the action of some inorganic additives on the protection of some multivalent ions during radiolysis of their aqueous solutions. The results showed that protection is most probably due to the competition reactions of the multivalent ions and the additive for the oxidizing or reducing species formed during water radiolysis<sup>(4-8)</sup>.

In the present work, a series of some organic additives have been used to investigate their capability in inducing valency stabilization of polyvalent iron ions when subjected to extended gamma irradiation periods. The results showed that the efficiency of valency stabilization depends on the amount and chemical structure of the organic additive used.

### ***Experimental:***

In the present work, radiolysis of aqueous systems of some iron ions in the presence of different types of organic additives has been undertaken. Thus, the radiolytic behaviour of Fe(II) or Fe(III) systems in the presence of a series of different classes of organic compounds comprising alcohols, aldehydes and acids, has been studied in detail. The effect of the additive concentration in the medium on the prevailing redox reactions of the polyvalent ion in the irradiated systems have been particularly treated.

#### ***1- Chemicals and Materials:***

Extra pure ferrous ammonium sulphate ( $\text{FeSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ ), ferrous sulphate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ), ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ ) were obtained from May and Baker (M & B) Co. LTD., and the British Drug House (B.D.H.) England.

Chemically pure methanol, ethanol, n-propanol and n-butanol were obtained from Camberian Chemicals, England. Acetaldehyde, Propionaldehyde and Butyraldehyde were supplied from Prolabo Co., Paris. Formic acid, chemically pure 100%, Sp.g. 1.231 was also obtained from Prolabo, France, Acetic acid for analysis, 99-100% sp.g. 1.055-1.050 was obtained from Fein Chemie K-H. Kallies KG, West Germany. Propionic acid, 99% was obtained from B.D.H. Co. England. All these chemicals except alcohols were used without further purification. All alcohols were distilled twice over freshly ignited and cooled CaO.

Analytical grade chemicals such as 1.10, phenanthroline (M.W. 180.21) were obtained from B.D.H. England. Sulphuric acid (98%); sp. g. 1.84, hydrochloric acid (35-37%), sp. g. 1.18, were also obtained from B.D.H. England.

All other chemicals were of the analytical grade reagents and were used without further purification.

## **2- Equipments:**

All pH measurements were carried out using an Orion Research pH meter model 616 A/ digital ion analyser with a combined glass-calomel electrode

Spectrophotometric measurements, were carried out using a Shimadzu UV-VIS double beam spectrophotometer type UV-210A. Glass or quartz cells were used whenever necessary

Potentiometric titrations were carried out using a Radiometer pH meter type PO3 with Pt and saturated Calomel electrodes.

## **3- Preparation of solutions:**

All solutions were prepared using double distilled water. The water was boiled then cooled and stored in stoppered glass flasks.

### **Preparation of iron solutions:**

#### **a) Preparation of Fe (II) solution:**

A.R.  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  crystals were washed twice with double distilled water followed by A.R. acetone and then dried by heating at  $50^\circ\text{C}$  for a few minutes. Exactly 2.7803 g of the purified ferrous sulphate were weighed and dissolved in about 300 ml of freshly boiled and cooled bidistilled water. The solution was quantitatively transferred to a 1 liter flask together with 22.2 ml cone.  $\text{H}_2\text{SO}_4$ , after being diluted with bidistilled water in 400 ml water. The resultant solution was then completed to the mark to give approximately 0.01N Fe(II) solution in 0.8N  $\text{H}_2\text{SO}_4$ .

The exact ferrous ion concentrations was determined titrimetrically with a standard (exactly about 0.1N) potassium permanganate solution prepared as described in detail elsewhere. The end point was determined potentiometrically

#### **b) Preparation of Fe(III) solution:**

About 0.01N Fe(III) solution was prepared by dissolving 3.999 g  $\text{Fe}_2$

(SO<sub>4</sub>)<sub>3</sub> 9H<sub>2</sub>O in hot bidistilled water. The resultant solution was filtered and the filtrate was introduced into a one litre volumetric flask together with 22.2 ml conc. H<sub>2</sub>SO<sub>4</sub> previously diluted to 400 ml and the resultant solution was then completed to the mark with double distilled water to give a solution containing 0.8N. H<sub>2</sub>SO<sub>4</sub>. The exact concentration of ferric ions in the solution was titrimetrically determined against a standard EDTA solution using tiron indicator at pH~2.5 at 40-50°C. At the equivalence point the solution turned from green to yellow.

#### **4- Preparation and Irradiation of Sample:**

The irradiated samples were prepared by introducing 5 mls of 10<sup>-2</sup> M Fe<sup>2+</sup> or Fe<sup>3+</sup> in 0.8N H<sub>2</sub>SO<sub>4</sub> together with the necessary amounts of different organic additives and the solutions were completed to the mark in 50 ml volumetric flasks. The resultant solutions were introduced into glass irradiation tubes (15 cm long and 2.5m diameter) and provided with a neck 1 cm in diameter with a ground glass stopper.

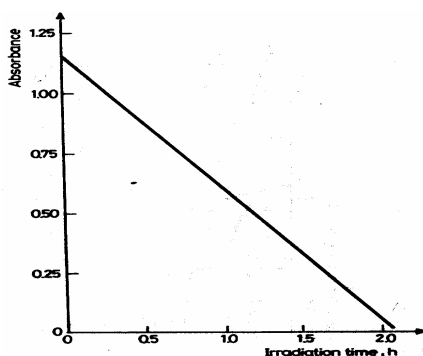
Irradiation of samples was carried out using a Canadian Co<sup>60</sup> gamma cell-220 for extended time periods. The irradiation dose of the irradiator was occasionally checked by the ferrous sulphate method. Samples were withdrawn at intervals and analysed.

During irradiation care was always taken to keep the position of the irradiation tubes unchanged along the whole irradiation period.

#### **Analysis of Irradiated Solution:**

In the present work, concentration of the Fe<sup>2+</sup> was followed spectrophotometrically using 1, 10 phenanthroline method<sup>(9)</sup>.

## **RESULTS**



**Fig: (1): Radiolytic decay of 10<sup>-3</sup>M Fe(II) solution in the presence of 0.08N H<sub>2</sub>SO<sub>4</sub> (Gamma-dose rate – 310 Gy/hr)**

$\text{Fe}^{2+}$  ions are known to be rapidly oxidized in gamma irradiated acidic solutions. Figure 1 shows that a  $10^{-3}\text{M}$   $\text{Fe}^{2+}$  acidic solution was completely oxidized in about 2 hours upon using a gamma dose rate of 310 Gy/h i.e. after absorbing about 620 gray<sup>(7)</sup>.

The role of different organic additives in the valency stabilization of iron ions during gamma irradiation, in presence of increasing amounts of organic acids, aldehydes and alcohols was studied by following the iron ion concentration spectrophotometrically on increasing gamma irradiation doses.

The results obtained are shown graphically in figures 2-7.

From these figures it is clear that most additives exerted a protective effect on  $\text{Fe}^{2+}$  ions for extended time periods. Extent of protection was dependant on the structure and concentration of the organic additive.

From the results shown graphically in figures 2-7 it could be observed that the organic additives used have different valency stabilization patterns of  $\text{Fe}^{2+}$ . Thus acids showed a single protection period while aldehydes and alcohols showed more than one valency stabilization periods.

In case of organic acid addition to  $\text{Fe}^{2+}$  ions ( Fig 2) it could be observed that in the protection process, three stage were evident namely oxidation, reduction and an extended steady protection stage in which  $\text{Fe}^{2+}$  concentration remained almost constant. At the end of the protection period the concentration of  $\text{Fe}^{2+}$  decreased gradually due to oxidation of prevailing  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

In case of  $\text{Fe}^{3+}$  system (fig 3)  $\text{Fe}^{3+}$  is first gradually reduced at a lower rate to  $\text{Fe}^{2+}$  before the steady valency stabilization state was reached at the end of which  $\text{Fe}^{2+}$  is oxidized back to  $\text{Fe}^{3+}$ .

Other organic additives showed a rather similar behavior (fig 4-7). Aldehydes showed two protection periods while alcohols showed also two protection periods the first of which was greater than in case of aldehydes, This could be attributed to the fact that aldehydes are oxidized to the corresponding acid then the acids were completely decomposed.

In case of alcohols the protection takes place through oxidation of alcohols to the corresponding aldehydes and then through further oxidation of aldehydes into acids. The alcohol/aldehyde protection overlaps with the aldehyde/acid protection forming a single valency stabilization stage. This is

followed by the acid protection stage which is rather longer and extends until the end of the acid existence when  $\text{Fe}^{2+}$  is gradually changed until  $\text{Fe}^{2+}$  is almost completely changed to  $\text{Fe}^{3+}$ .

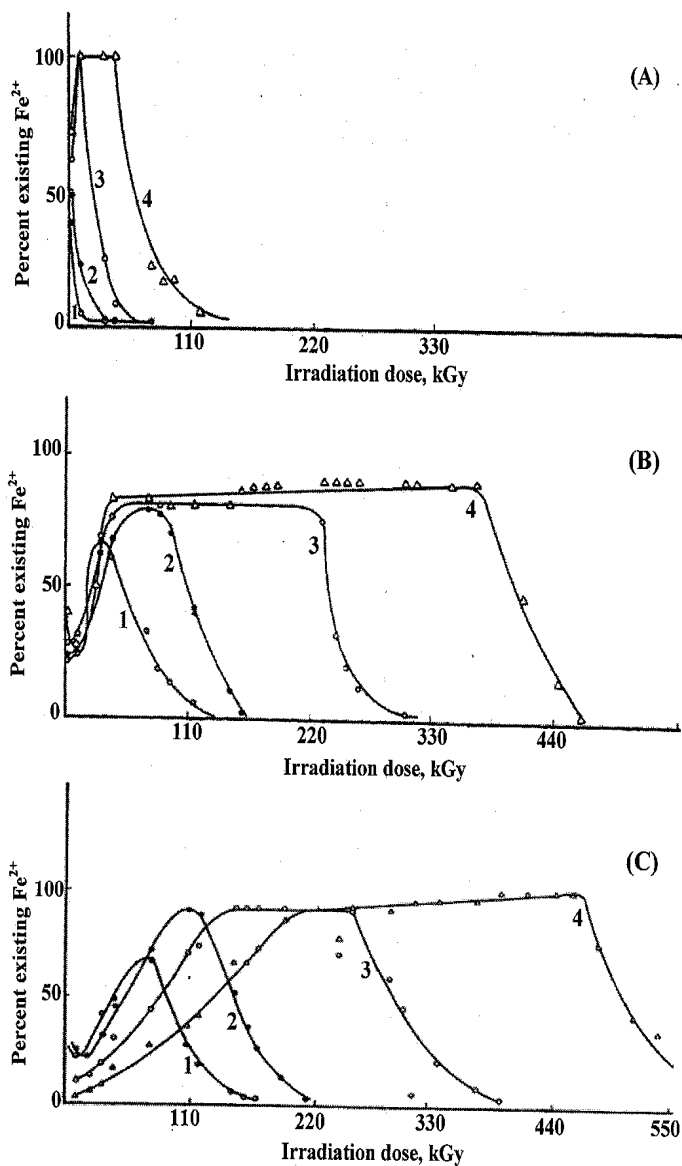


Fig. (2) Percent existing  $\text{Fe}^{2+}$  in  $\gamma$ -irradiated  $10^{-3}$  M  $\text{Fe}^{2+}$  Solutions ( $0.08 \text{ NH}_2\text{SO}_4$ ) Containing  
 A- Formic acid B- Acetic acid C- Propionic acid; at various concentrations:  
 1-  $1.6 \times 10^{-3}$  M (●) 2-  $3.2 \times 10^{-3}$  M (x) 3-  $8.0 \times 10^{-3}$  M (○) 4-  $16.0 \times 10^{-3}$  M (Δ)

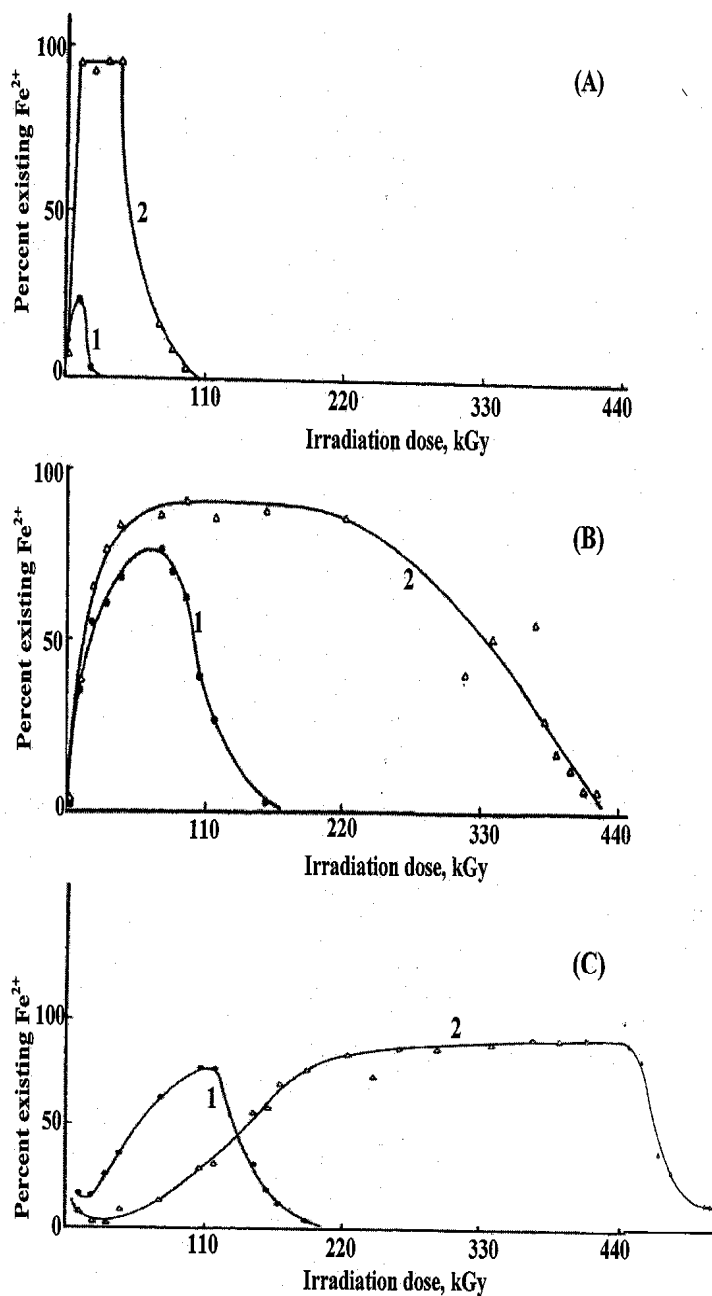


Fig. (3) Percent existing Fe<sup>2+</sup> in  $\gamma$ -irradiated  $10^{-3}$  M Fe<sup>3+</sup> Solutions (0.08 NH<sub>2</sub>SO<sub>4</sub>) Containing  
 A- Formic acid B- Acetic acid C- Propionic acid; at various concentrations:  
 1-  $3.2 \times 10^{-3}$  M (●) 2-  $16.0 \times 10^{-3}$  M (○)

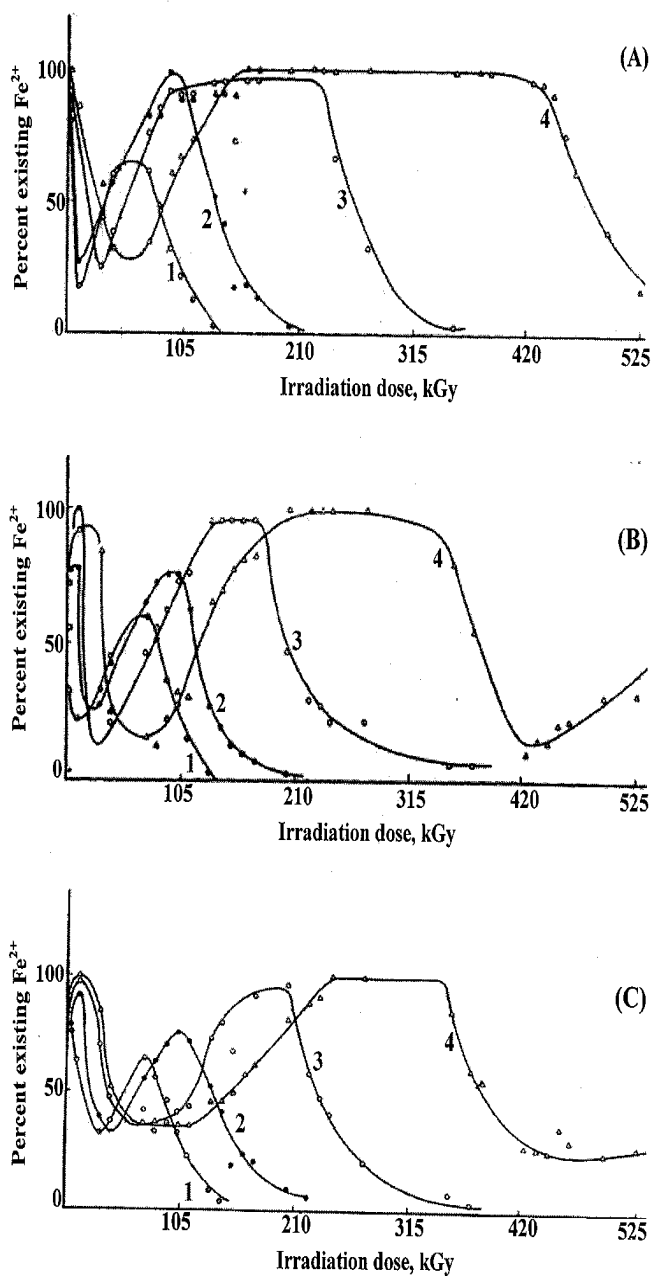


Fig. (4) Percent existing  $\text{Fe}^{2+}$  in  $\gamma$ -irradiated  $10^{-3}$  M  $\text{Fe}^{2+}$  Solutions ( $0.08 \text{ NH}_2\text{SO}_4$ ) Containing  
 A- Acetaldehyde B- Propionaldehyde C- Butyraldehyde; at various concentrations:  
 1-  $1.6 \times 10^{-3}$  M ( $\bullet$ ) 2-  $3.2 \times 10^{-3}$  M ( $\times$ ) 3-  $8.0 \times 10^{-3}$  M ( $\circ$ ) 4-  $16.0 \times 10^{-3}$  M ( $\Delta$ )



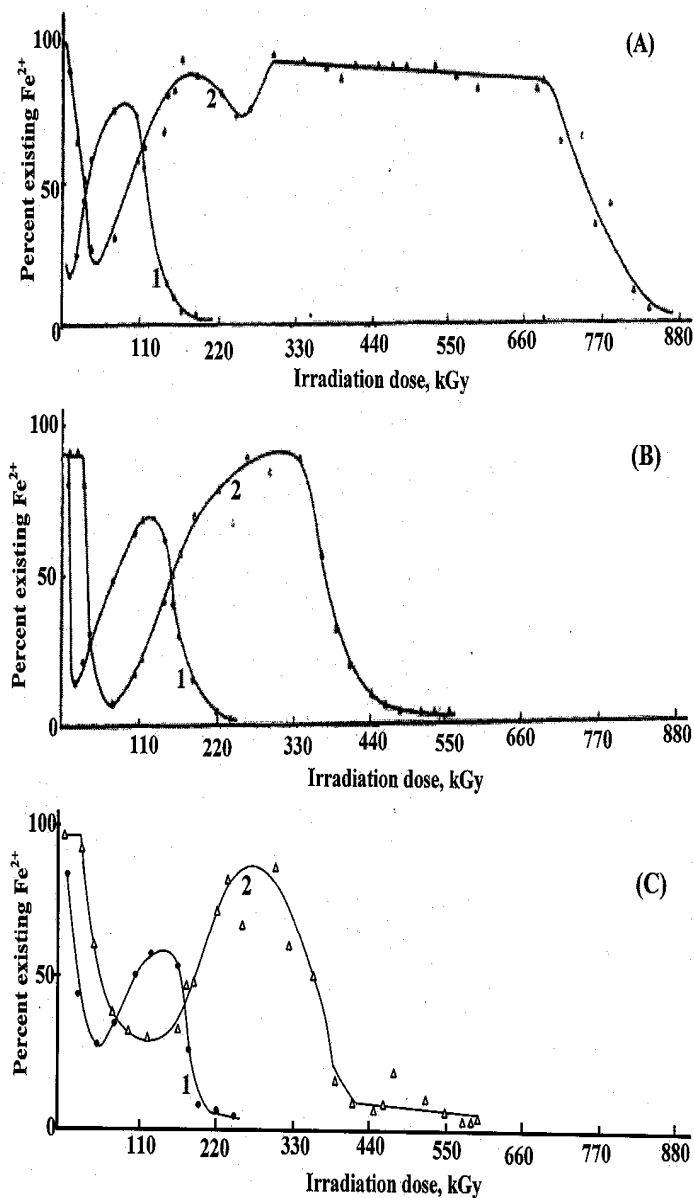


Fig. (5) Percent existing Fe<sup>2+</sup> in  $\gamma$ -irradiated  $10^{-3}$  M Fe<sup>3+</sup> Solutions ( $0.08$  NH<sub>2</sub>SO<sub>4</sub>) Containing  
 A- Acetaldehyde B- Propionaldehyde C- Butyraldehyde; at various concentrations:  
 1-  $3.2 \times 10^{-3}$  M (●) 2-  $16.0 \times 10^{-3}$  M (△)

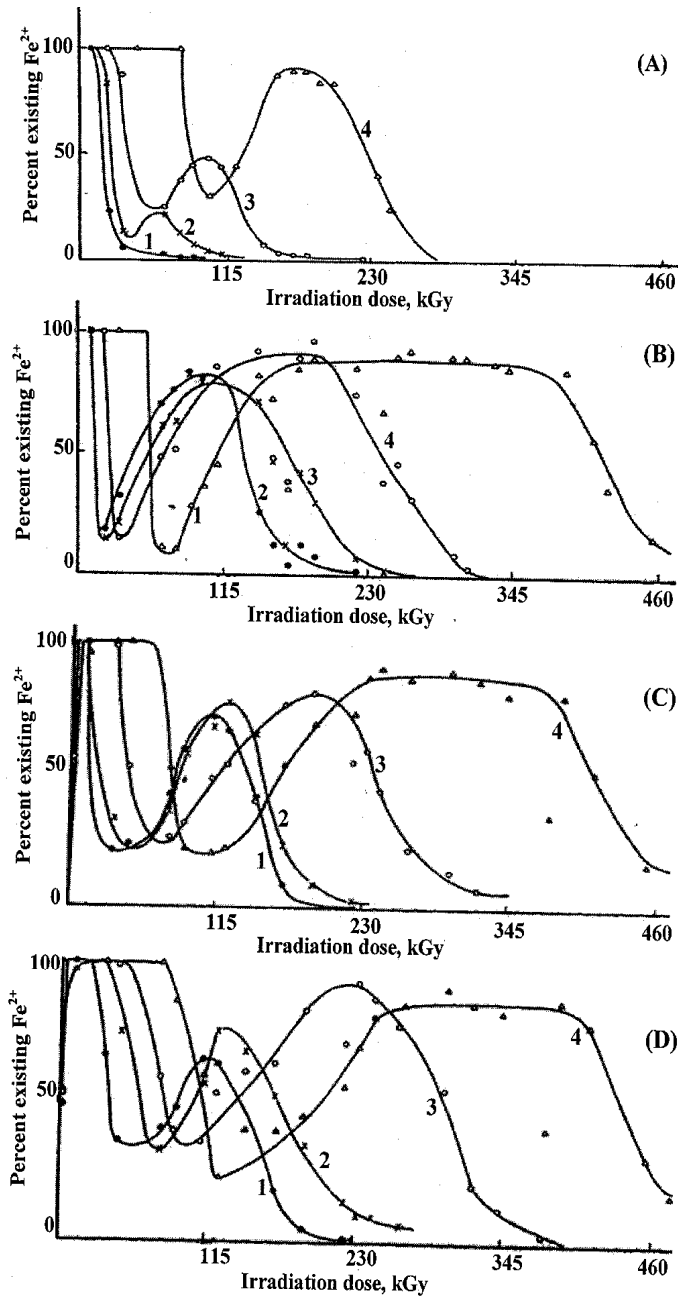


Fig. (6) Percent existing Fe<sup>2+</sup> in  $\gamma$ -irradiated  $10^{-3}$  M Fe<sup>2+</sup> Solutions ( $0.08 \text{ NH}_2\text{SO}_4$ ) Containing  
 A- Methanol B- Ethanol C- Propanol D- Butanol; at various concentrations:  
 1-  $3.2 \times 10^{-3}$  M ( $\bullet$ ) 2-  $4.8 \times 10^{-3}$  M ( $\times$ ) 3-  $8.0 \times 10^{-3}$  M ( $\circ$ ) 4-  $14.0 \times 10^{-3}$  M ( $\Delta$ )

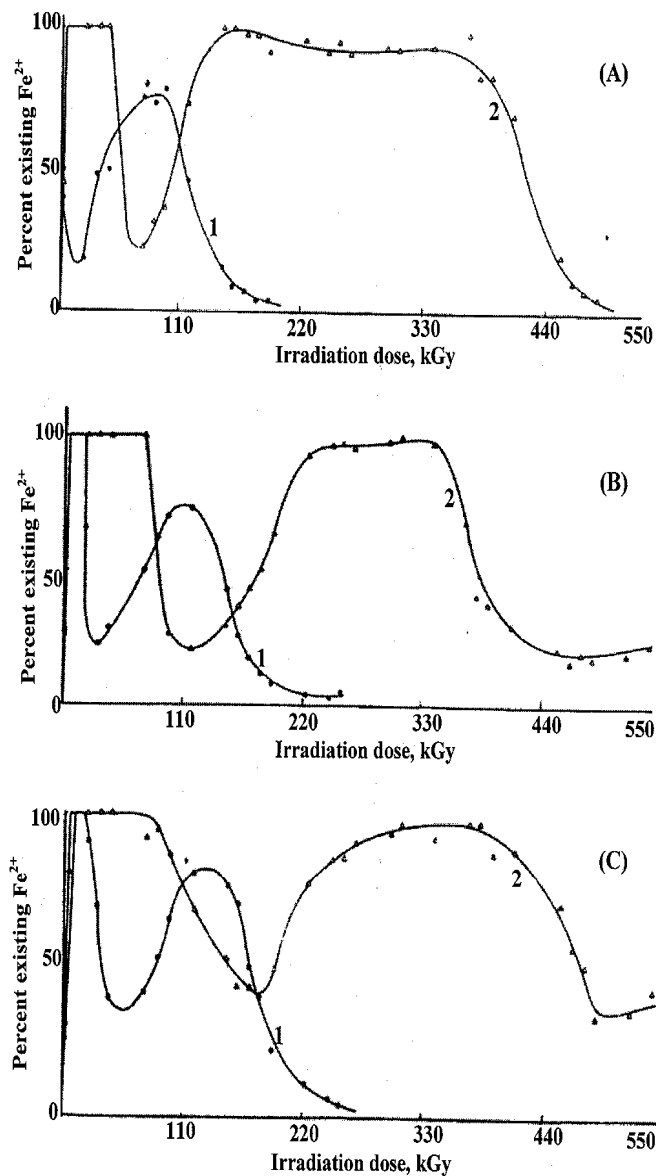


Fig. (7) Percent existing Fe<sup>2+</sup> in  $\gamma$ -irradiated 10<sup>-3</sup> M Fe<sup>3+</sup> Solutions (0.08 NH<sub>2</sub>SO<sub>4</sub>) Containing  
 A- Ethanol B- Propanol C- Butanol; at various concentrations:  
 1- 3.2 x 10<sup>-3</sup> M (●) 2- 16.0 x 10<sup>-3</sup> M (○)

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