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**RADIOLYSIS OF COBALT(III)-1,2 BIS(BETA-AMINOETHOXY)ETHANE
N,N,N',N' SODIUM SULFUNATE TRIACETIC ACID CHELATE
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ABSTRACT

The publication demonstrates chelation studies of cobalt(III) with 1,2 bis(beta-aminoethoxy)ethane N,N,N',N'sodium sulfonate triacetic acid (ASTA). The results showed the effectiveness of ASTA as a chelating agent by molar ratio, continuous variation and slope ratio methods. Stable complex 1:1 was formed at pH from 6.0 to 10.5. Solutions of Co-ASTA chelate of different molar ratios at pH 6.5 and 8.0 were irradiated by different gamma radiation doses. The results showed a linear decrease of absorbance with dose which can be utilized as a dosimeter for weak dose rate measurement in the studied range. A proposed radiolytic mechanism is discussed. The degradation of ligand has been related to hydroxyl radical attack.

KEYWORDS

Gamma radiation / Chelate / Effect of radiation / Complex / Polyamino polycarboxylic acids / Cobalt / Radiolysis .

INTRODUCTION

The general methods of internal decontamination use the chelating agents [1,2]. The polyamino polycarboxylic acids are excreted without being metabolized and form stable chelates with rare earths [3]. Ethylene Diamine Tetraacetic Acid (EDTA) [3], Diethylene Triamine Pentaacetic Acid (DTPA) and other polyamino polycarboxylic acids [4], are among these acids that are used for internal and external radioactive decontamination.

The effectiveness of the chelating agent as decontaminant is inversely proportional with the time interval between the incorporation of radionuclides and treatment. It depends also on the ability of biological compartments to bind them more tightly, the chelate stability constant, degree of polymerization of radioelement and pH [5,6].

Since chelation may be utilized for the internal decontamination of radioactive cobalt species from body, therefore it is important to study the effect of gamma rays on the formed Co-ASTA chelate.

In dilute aqueous solutions, the main radiolytic reactions originate from interaction of created radiolytic species of water with the existing chelate of cobalt. The main created species during radiolysis of water are $\cdot H$, $\cdot OH$, H_2 , H_2O_2 and hydrated electrons [5].

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EXPERIMENTAL PROCEDURE

All chemicals used were of analytical grade. The pH of the chelate solutions were adjusted by PW 9409 pH Meter using sodium hydroxide (free from carbonate) and hydrochloric acid. The stock solution of ASTA and CoCl_2 were standardized [8,9]. 0.25 ml H_2O_2 was added during mixing CoCl_2 with ASTA solutions, both in predetermined concentrations to obtain the required preparations for molar ratio, continuous variation and slope ratio methods [4,5,9]. The absorbance measurements were done using Cecil CE 599 Universal Automatic Scanning Spectrophotometer 24 hours after preparation of chelate solutions. The stability constant of the formed chelate was determined.

Co(III) : ASTA chelates were prepared as follows : solutions of 1×10^{-2} M Co(III) were mixed with equal volumes of ASTA solutions of concentrations 1×10^{-2} and 2×10^{-2} M to get a molar ratio $[\text{Co(III)}] / [\text{ASTA}]$ equals 1/1 and 1/2. The two series of solutions were prepared at pH 6.5 and 8.0. The solutions were irradiated by gamma radiation for different doses ranging from 0 - 895 Gy with dose rate equals $3.114 \text{ Gy} \cdot \text{min}^{-1}$. The spectra of irradiated solutions were obtained and G-values were determined.

RESULTS AND DISCUSSION

Figure (1) shows absorbance spectra of 2×10^{-2} M ASTA, 2×10^{-2} M Co(II) and the mixture of both at pH 6.5. Absorbance spectra of Co(III) : ASTA was obtained after addition of H_2O_2 with two peaks. Figure (2) shows the validity of Beer's law for the formed chelate. Figure (3) demonstrates the variation of absorbance at $\lambda = 565 \text{ nm}$ as a function of pH for Co(III) : ASTA chelate. The figure indicates that the complex was completely formed at $6 \leq \text{pH} \leq 10.5$.

The ratio of Co(III) to ASTA of the formed chelate at pH 7.5 and 9.5 was performed by : Molar ratio method where $[\text{Co(III)}]$ or $[\text{ASTA}]$ was kept constant at 0.5×10^{-2} M, Continuous variation method where the total concentration was equal to 2×10^{-2} M and Slope ratio method where the excess concentration of either Co(III) or ASTA was 3×10^{-2} M. The results in figures (4,5,6,) show that 1:1 complex was formed. Stability constant K was calculated [4] and $\log K$ was found 21.91.

Figure (7) shows the absorbance spectra of irradiated Co(III) : ASTA chelate for different doses at pH 6.5 and 8 for molar ratio $[\text{Co(III)}] / [\text{ASTA}]$ equals 1/1 and 1/2. The absorbance of the spectra decreased with increase of absorbed dose. The radiation yields (G-values) were determined and found for 1/1 at chelate 1.40 & 1.73 and for 1/2 chelate 1.3 & 1.45 at pH 6.5 & 8.0 for each respectively.

Figure (8) shows that the decrease in the absorbance with the absorbed dose is linear and thus these results can be utilized as a dosimeter for the studied dose range.

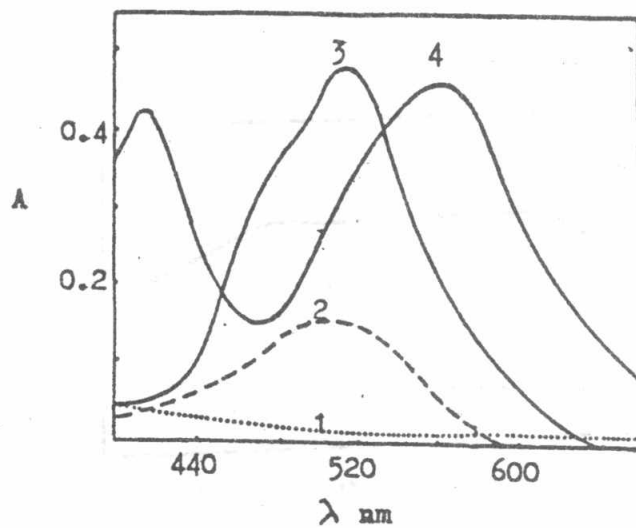


Figure (1) : Absorption spectra of ASTA 5×10^{-2} M [1], Co(II) 5×10^{-2} M [2], Co(II):ASTA 5×10^{-2} M [3] and Co(III):ASTA 2.5×10^{-2} M [4].

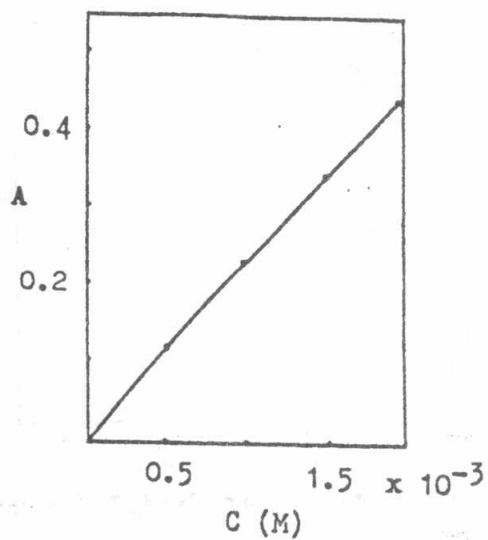


Figure (2) : Variation of the absorbance at pH 7.5 and $\lambda = 565$ nm with Co(III) : ASTA concentration .

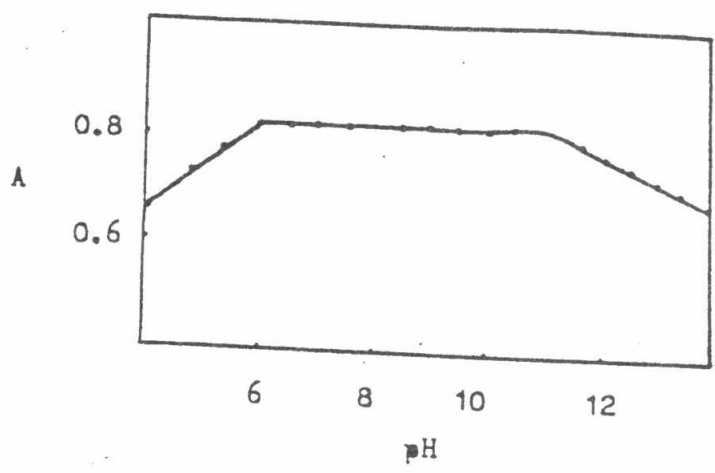


Figure (3) : Variation of the absorbance at $\lambda = 565$ nm and the chelate concentration of 5×10^{-3} M as a function of pH .

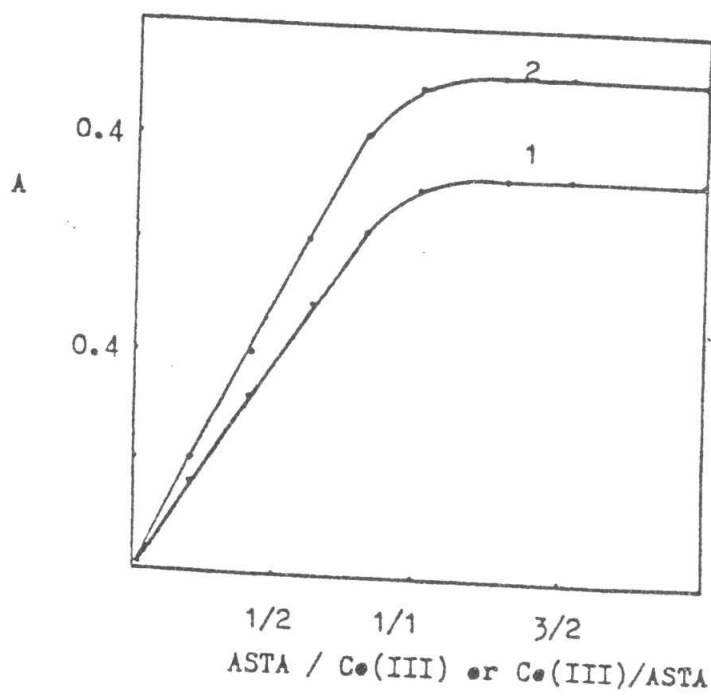


Figure (4) : Variation of the absorbance at $\lambda = 565$ nm and constant concentration of ASTA or Co(III) of 2×10^{-3} M , with molar ratio $[\text{Co(III)}] / [\text{ASTA}]$ [1] & $[\text{ASTA}] / [\text{Co(III)}]$ [2] at pH 7.5 and 9.5.

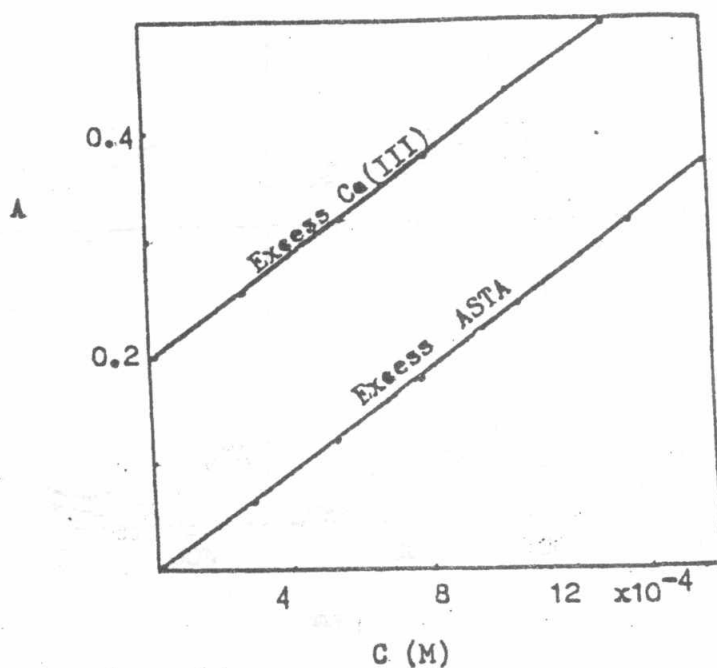


Figure (5): Variation of the absorbance at $\lambda = 565 \text{ nm}$ with molar concentration of Co(III) or ASTA in the excess of the other at concentration of $2 \times 10^{-2} \text{ M}$ at pH 7.5.

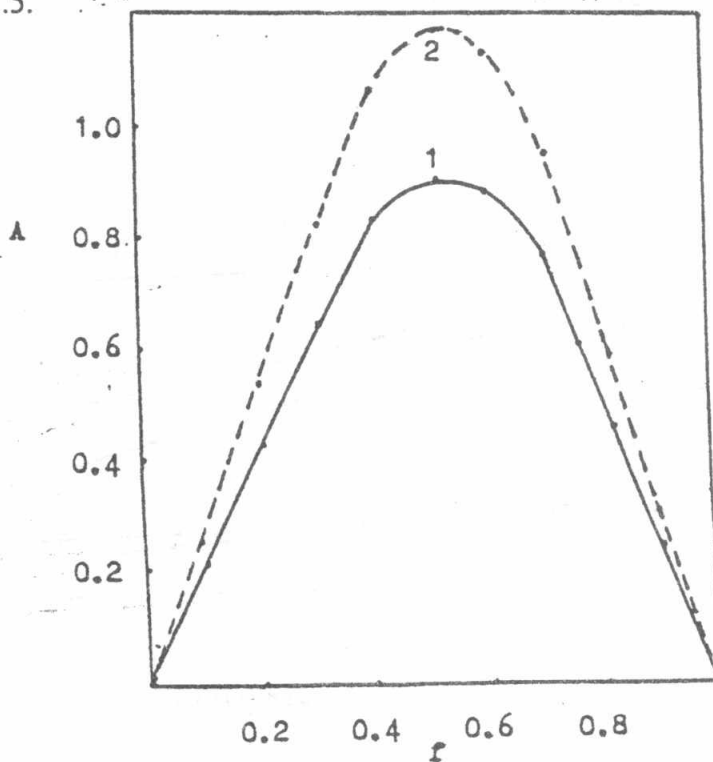


Figure (6): Variation of absorbance at $\lambda = 565 \text{ nm}$ at pH 7.5 [1] & pH 9.5 [2] as a function of $\frac{[\text{ASTA}]}{[\text{ASTA}] + [\text{Co(III)}]}$. Where $[\text{ASTA}] + [\text{Co(III)}]$ equals $5 \times 10^{-3} \text{ M}$.

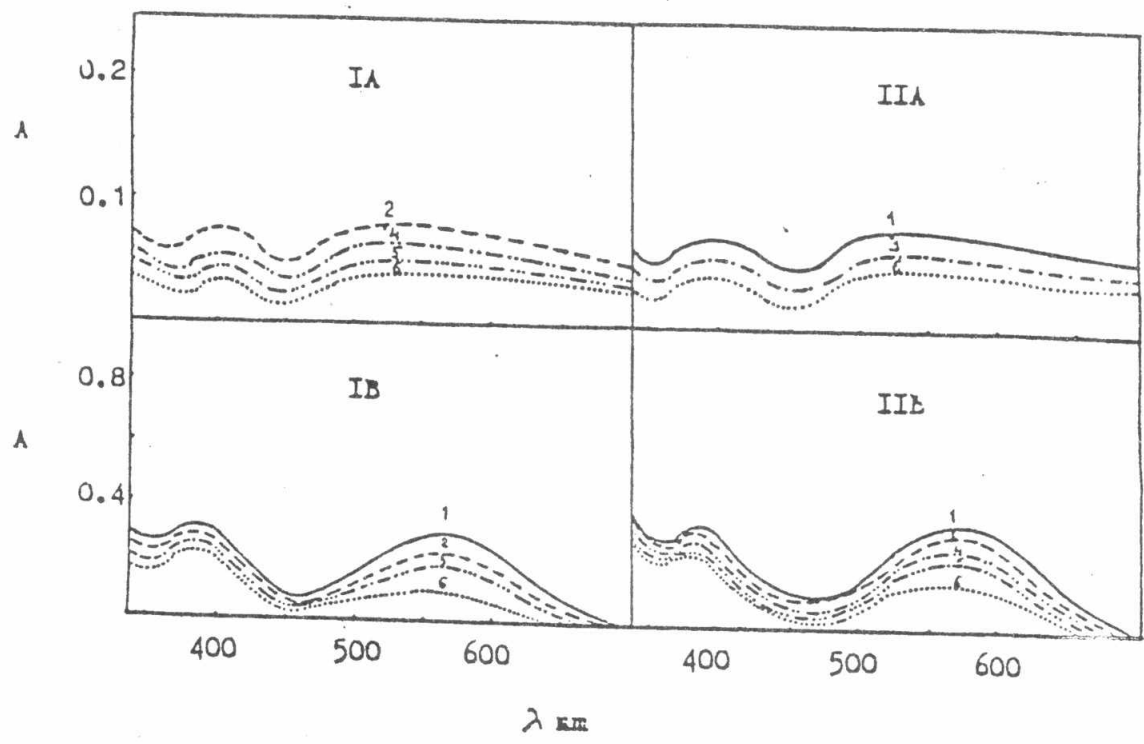


Figure (7) : Absorption spectra of 1/1 [I] and 1/2 [II] chelates at pH 6.5 (A) and 8.0 (B) irradiated at different irradiation doses of 0 [1] & 66 [2] & 396 [3] & 440 [3] & 505 [5] & 895 Gy [6].

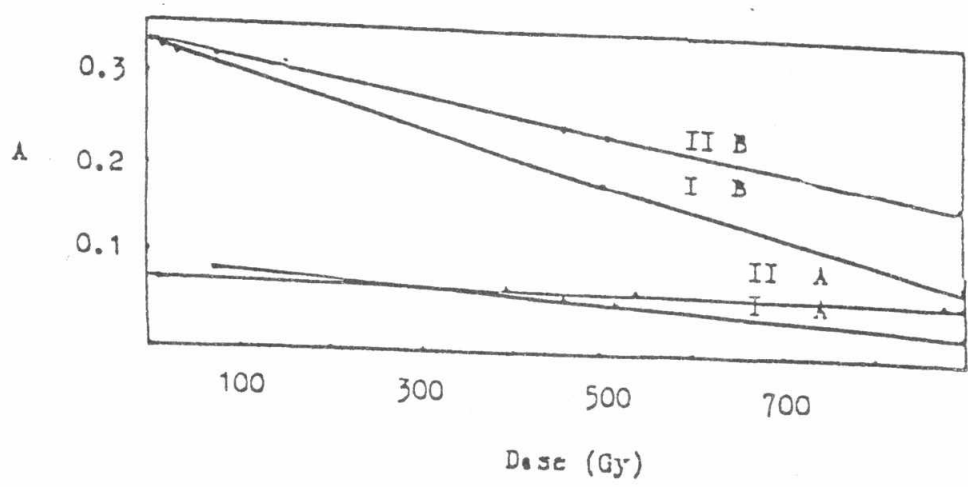


Figure (8) : Variation of the absorbance at $\lambda = 565$ nm with absorbed dose for chelate 1/1 [I] and 1/2 [II] at pH 6.5 (A) and pH 8.0 (B).

As has been reported in radiolysis of metal chelates of polyamino polycarboxylic acids [10,11]

it is possible to suppose that .OH radicals (that are created from radiolysis of water) attack the chelating agent and Co(III) in both acidic and neutral mediums. Attack of hydroxyl radical to chelating agent leads to removal of hydrogen atom from the agent causing its degradation. Attack of hydroxyl radical for the same molecule may produce hydrogen radical that may reduce Co(III) to Co(II). As a result, an attack of two hydroxyl radicals may decompose Co(III):ASTA to simple Co(II). The obtained G-values agree with that proposal. Similar mechanism was proposed [5,10,11,12,13].

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