THE CHEMISTRY OF
FERROUS-FERRIC DOSIMETERS

by
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STATEMENT BY AUTHOR

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ABSTRACT

Aqueous solutions of potassium ferrioxalate and ferric bathophenanthroline were evaluated as chemical dosimeters. The behavior and sensitivities of these systems were investigated and optimized by varying concentrations, pH, and organic additives. The dosimeters were irradiated with X-rays produced by bombarding a tungsten target with 0.875 MeV electrons. The production ferrous ions was determined colorimetrically with bathopenanthroline (4,7-diphenyl-1,10-phenanthroline).

These dosimeters were examined over the range of 20 rad to 20 K rad. The quantum efficiencies ($\gamma$) and the G-values found were:

$$\begin{align*}
\text{Fe(Ox)}_3 & \quad \text{Fe(Bph)}_3 \\
\gamma: & \quad 87.8 \quad 1.48 \times 10^3 \\
G: & \quad 0.141 \quad 2.51
\end{align*}$$

The minimum doses detected were 1,000 rad for the ferrioxalate and 20 rad for the ferric bathophenanthroline system.
INTRODUCTION

A chemical dosimeter measures the amount of radiation absorbed in a system by means of a chemical reaction induced by the absorbed radiation. The mechanisms involved in the absorption and interactions of x and gamma radiation with the chemical dosimeter, are the subjects of considerable interest in the field of radiation chemistry.

Historically, radiation induced chemical reactions had been observed as early as 1817 in experiments with hydrogen and chlorine. One of the first calibrated actinometers (a device which measures the total amount of visible and uv light absorbed by a material) consisted of an aqueous solution of uranyl oxalate (Leighton and Forbes, 1930). The system was investigated by irradiating with light in the visible and near uv range (2500-4500 Å).

Some other systems which have been investigated are mixtures of nitric acid and various ketones, and the decomposition of diazonium salts with phosphorous acid (Korblum, et al., 1950). Mixtures of halogenated hydrocarbons and water were also investigated as possible chemical dosimeters (Taplin and Douglass, 1956). The products of irradiation in these systems include a water soluble acid which may be measured colorimetrically with the use of suitable indicators.

In 1935, Fricke and Hart used an aerated ferrous sulfate solution to obtain reliable x-radiation measurements at low dose rates. This system (now known as the Fricke Cell) is an attempt to utilize the oxidizing ability of irradiated aqueous solutions. Parallels and
comparisons of the Fricke Cell to the systems investigated in this work will be developed later.

The systems investigated in this work were aqueous solutions of potassium ferrioxalate and ferric bathophenanthroline. The original ferrioxalate work was done by Allmand and Webb in 1929. Their observations of photochemical reactions were made using various wavelengths of mixed and monochromatic visible light. In following years, the discovery of more sensitive analytical indicators led to further refinement of the process, resulting in greater sensitivity (Parker, 1953). Ensuing investigations (Parker and Hatchard, 1956), eliminated many of the previously underdetermined variables and established a reliable, constant quantum efficiency for the system.

The ferric bathophenanthroline system had not been previously investigated as a possible chemical dosimeter. Investigations of the response of other systems (e.g., ferric \( \text{1,10 phenanthroline} \)) to uv and visible light have been carried out (Baxendale and Bridge, 1955). Bathophenanthroline, \( \text{4,7-diphenyl, -1,10-phenanthroline} \), was shown to be a very sensitive detector of ferrous iron in aqueous solution (Smith, et.al., 1952). The sensitivity may be further increased by extracting the colored complex into an organic solvent such as isoamyl or n-hexyl alcohol.

Several aqueous ferric solutions were exposed to various radiation environments to investigate the radiolytic reduction of ferric ions. The object of this work was to devise a sensitive chemical dosimeter in which ferric ions were reduced in aqueous solutions. The chemical procedures and techniques developed, optimized the sensitivity.
of the dosimeter to the effects of x and gamma radiation. In the investigation of these chemical systems, an understanding of the mechanisms of the reactions involved was developed.
THEORY

When a molecule absorbs energy, several distinct results may occur. The following potential energy diagrams help explain these possibilities (Moore, 1950). Fig. 1 shows the simple transition from a stable ground to stable excited state. In Fig. 2, the transition is to an unstable excited state which dissociates immediately. Absorption of sufficient quanta in excess of the excited state binding energy will also lead to dissociation as shown in Fig. 3. In Fig. 4, the initial transition is to a stable excited state which is intersected by the potential energy surface of an unstable state, and the molecule can dissociate after a delay of only several vibrations.

When radiation is absorbed in water (the major constituent of any aqueous chemical dosimeter), oxidants are formed (Allen, et.al., 1952) e.g., OH, HO_2, H_2O_2 as shown by Equations 1 through 3.

\[ \text{hv} + \text{H}_2\text{O} \rightleftharpoons \text{H} + \text{OH} \]  
\[ \text{H} + \text{O}_2 \rightleftharpoons \text{HO}_2 \]  
\[ \text{HO}_2^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2 \]

The Fricke Cell is based on the oxidation of ferrous ions in an air saturated sulfuric acid solution as indicated in Equations 4 through 6.

\[ \text{Fe}^{+2} + \text{OH} \rightleftharpoons \text{Fe}^{+3} + \text{OH}^- \]  
\[ \text{Fe}^{+2} + \text{HO}_2 \rightleftharpoons \text{Fe}^{+3} + \text{HO}_2^- \]  
\[ \text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightleftharpoons \text{Fe}^{+3} + \text{OH}^- + \text{OH} \]
Fig. 1  Direct excitation of a molecule to a stable excited state.

Fig. 2  Direct excitation of a molecule to an unstable excited state.

Fig. 3  Molecular excitation where energy is absorbed in excess of the stable excited state binding energy thus leading to dissociation.

Fig. 4  Direct excitation to a stable excited state which is intersected by the potential energy surface of an unstable excited state.
In addition to these reactions, there also exists another stage of internal oxidation (Weiss, 1935) with the formation of $O_2^-$ by electron transfer:

$$\text{Fe}^{+2} + O_2 \rightarrow \text{Fe}^{+3} + O_2^- \quad (7)$$

The yield of ferric ions in the Fricke dosimeter is dependent on the presence of oxygen in the solution. In large doses (50 kr), the available oxygen is consumed and the yield drops off. At very low doses, the system is limited by the sensitivity of the method of detection.

The reduction of ferric ions in aqueous solutions by radiation is opposed by all of the mechanisms which favor the Fricke dosimeter. However, since photosensitive ferric compounds are available, as well as highly sensitive analytical methods for the detection of ferrous ions, the system merits investigation as a possible chemical dosimeter.

A possible reduction mechanism for a photosensitive complex $C^{+3}$ may be represented by:

$$C^{+3} \overset{h\nu}{\longrightarrow} (C^{+3})^* \quad k_1 \text{ activation} \quad (8)$$

$$\quad (C^{+3})^* + R \rightarrow C^{+2} \quad k_2 \quad (9)$$

$$\quad (C^{+3})^* + M \rightarrow C^{+3} \quad k_3 \text{ deactivation} \quad (10)$$

where:

- $C^{+3}$ is a photosensitive ferric complex
- $k_n$ is the rate constant of the $n^{th}$ reaction
- $R$ is an easily oxidized organic species such as $\text{HCOOH}$
- $M$ is any species capable of removing excitation energy.
In addition to the described reactions, there is a primary "dark" or thermal reaction:

\[
\text{C}^+^2 \rightarrow \text{C}^+^3 + e^- \quad k_4 \quad \text{oxidation} \quad (11)
\]

The rate of this reaction is dependent on the properties of the medium, particularly the pH and concentration of species which have a much lower oxidation energy than C\(^{+2}\). In order to produce an appreciable amount of C\(^{+2}\), then \(k_2 \gg k_3 + k_4\). This may be accomplished by selecting the proper \(R\) species and minimizing the amount of \(M\) in the system. For the two systems investigated in this work, \(R\) is present as oxalate ions in the potassium ferrioxalate system and as formate ions in the ferric bathophenanthroline system.

The selection of ferrioxalate as a chemical dosimeter system was based on investigations by Parker (Parker, 1952) who used potassium ferrioxalate as an actinometer. This research was performed with monochromatic light and a quantum efficiency greater than one was observed. Parker postulated the probable reaction mechanisms illustrated in Fig. 5.

The sensitivity of the ferrioxalate dosimeter depends primarily on the analytical detectability of ferrous ions. For this purpose, bathophenanthroline (which will be abbreviated hereafter as Bph)* was selected as the colorimetric indicator for ferrous iron. This organic chelating agent forms a red tris complex with ferrous ions and has been shown to be capable of detecting \(10^{-2} \mu\) mole/ml (Smith, et.al., 1952) of

* The definitions of all chemical and radiation terms and abbreviations are presented in the glossary to aid the reader.
Fig. 5  The possible stages of the photo-decomposition of ferrioxalate by direct excitation.
ferrous iron. Some of the advantages of Bph over 1,10 phenanthroline, which was used by Parker, are that the ferrous complex molar extinction coefficient is increased from 11,100 to 22,400 and that the Fe(Bph)$_3$ could be extracted from aqueous solution with organic solvents such as isoamyl alcohol. There are no known interferences by either metallic cations or common anions with the color of the ferrous Bph complex. The Bph molecule and ferrous complex are shown schematically in Figs. 6 and 7.

A literature search for information on the ferrous complexes with phenanthroline derivatives revealed that ferric compounds of phenanthroline could be photoreduced (Baxendale and Bridge, 1955). Equations 12 through 16 show the various reactions in an acidic iron phenanthroline (Ph) aqueous system (Kolthoff, et.al., 1948). K is the equilibrium constant for the reaction.

\[
\text{FePh}^+ \Leftrightarrow \text{Fe}^+ + 3\text{Ph} \quad K = 8 \times 10^{-15} \tag{12}
\]

\[
\text{FePh}^+ + \text{Fe}^2 \Leftrightarrow \text{Fe}^+ + \text{FePh}^+ \tag{13}
\]

\[
\text{FePh}^+ + 3\text{H}^+ \Leftrightarrow \text{Fe}^+ + 3\text{HPh} \tag{14}
\]

\[
\text{FePh}^+ + 6\text{H}^+ \Leftrightarrow \text{Fe}^+ + 3\text{H}_2\text{Ph} \tag{15}
\]

\[
\text{FePh}^+ \Leftrightarrow \text{Fe}^+ + 3\text{Ph} \quad K = 5 \times 10^{-22} \tag{16}
\]

It may be assumed that the Bph complex behaves in a manner similar to 1,10 Ph except for an increase in basicity of the Bph molecule due to the phenyl substitution. Recent investigations of methyl derivatives of phenanthroline have shown an increase in ferrous complex stability over that of 1,10 Ph. This was attributed to the increase in basic strength.
The structural formula for bathophenanthroline (4,7-diphenyl-1,10-phenanthroline).

A stereochemical form of Fe(Bph)\(^{2+}\) where Bph is bathophenanthroline.
of the substituted Ph over the unsubstituted Ph. Therefore, it is expected that ferrous Bph complex would have a greater stability constant than the corresponding 1,10 Ph complex.

When using Ph for ferrous iron detection in aqueous solutions, a pH of 2.5 to 3 is required and the ferrous ion concentration must be less than the concentration of free phenanthroline (Kolthoff, et al., 1950). The relationship between the free Ph concentration and the relative amount of the red tris ferrous complex is shown in Fig. 8. The monophenanthroline complex formed is yellow and does not contribute to the red absorption at 533 μm.

![Fig. 8 Mole % of Fe²⁺, FePh⁺² and FePh³⁺ as a function of Ph concentration](image)

The actinometer experiments with ferrioxalate and ferric phenanthroline were reported to have a quantum efficiency of near unity. The investigations in this work were designed to validate the results of these experimentors using x and gamma radiation and to increase the sensitivity of the systems through the use of bathophenanthroline as a sensitive quantitative colorimetric indicator of Fe⁺² in the presence of Fe⁺³.
EXPERIMENTAL

Apparatus

The chemical dosimeter systems investigated were irradiated in two facilities, the University of Arizona's electron accelerator laboratory and a shielded lead brick cell containing a 3 mc Co\textsuperscript{60} source (Fig. 9).

The electron accelerator has the capability of producing 1.25 Mev electrons and a beam current of 10 ma. The samples to be irradiated were placed in a foamed plastic holder 10 inches from the X-ray target. A self calibrating ion chamber was placed directly behind the samples such that the center of the chamber was 3 inches from the center of the samples. A self shielded cable connected the chamber to a dose rate meter in the accelerator control room. The range of the meter was from 0.01 to 10 Kr/hr.

All of the irradiations in these experiments were performed with X-rays produced by bombarding a tungsten target with 0.875 Mev electrons. The spectrum of X-ray wavelengths obtainable from a tungsten target is shown in Fig. 11. The dose rate was read directly from the dose rate meter which had a quoted accuracy of \(\pm 5\%\) over the range of 0.01 to 10 Kr/hr. Allowances were made for irradiation occurring while bringing the machine up to power by starting the timer just prior to arriving at the desired dose rate. This problem does not arise in shut-down which is an instantaneous power cut-off procedure. During the irradiation
Fig. 9  The apparatus used for Co$^{60}$ irradiations. It was composed of lead brick having two channels open to the source. The distances between the source and samples was such that dose rates of 14.5, 8, 7.2, and 3.5 mr/hr at positions A, B, C, and D, respectively, were obtained.
time, the dose rate could be held constant to \( \pm 2\% \). In this manner, accurate doses may be obtained by control of the dose rate and irradiation time. The geometric relation (Fig. 10) between the target and samples was such that there was no detectable variation in X-ray intensity between sample positions. However, since there was a linear difference between the samples and the center of the ion chamber, the dose rate readings of the meter were not the actual dose rates that the samples were exposed to. An error of \( \pm 5\% \) in these readings was calculated assuming a point source and \( \sim 20\% \) absorption of X-rays by the samples. This error was incorporated in the values reported. The self shielding ability of the chamber cable was tested and found not to be affected by radiation fields in signal transmission.

Fig. 10  The geometry of the X-ray irradiation apparatus. Electron originating in the accelerator are collimated to strike the tungsten target.
Fig. 11 The characteristic X-ray spectrum for tungsten resulting from irradiation with 0.875 MeV electrons (Uhrey, 1918).
The low level Co\textsuperscript{60} irradiation source as shown in Fig. 9 was in an aqueous solution stored in a 100 ml volumetric flask. The samples to be irradiated were placed in the two channels leading from the central pig. The dose rates at the four positions, measured with a GM survey meter were 14.5, 8, 7.2, and 3.5 mr/hr. The entire assembly was constructed from lead brick and sheet. The Co\textsuperscript{60} gamma rays have energies of 1.33 and 1.17 Mev. The isotope has a half life of 5.27 yr and, therefore, does not vary significantly in strength during an exposure. The samples to be irradiated in all experiments were transferred into 30 ml test tubes. These tubes were painted on the outer surface with flat black paint and then wound with black electrical tape, since they were known to be sensitive to visible and ultraviolet light. The samples were then sealed with black rubber stoppers to insure a light tight container. All loading and chemical processing was done in a photographic darkroom under yellow-green wratten series OA safelight.

Color intensities and wavelengths of absorption peaks were measured on a spectrophotometer using a tungsten lamp and standard 1 cm quartz cells. Measurements were also made on a colorimeter at a wavelength of 533 m\textmu using standard optically clear test tubes. A pH meter was also used to measure the pH of many of the solutions.

Experiments With Ferrioxalate

The potassium ferrioxalate solution was prepared by dissolving 0.006 moles of K\textsubscript{3}Fe(Ox)\textsubscript{3} in one liter of 0.05 M H\textsubscript{2}SO\textsubscript{4}. The potassium ferrioxalate crystals were prepared by mixing 1.5 M solutions of analytic reagent (A.R.) grade potassium oxalate and ferric chloride in
a ratio of three to one. The precipitated potassium ferrioxalate was purified by recrystallizing three times from warm water and then dried at 45°C in air (Parker, 1955). Both crystals and solution are stable for long periods when prepared in the dark and stored in opaque containers.

A $10^{-3} \text{M}$ bathophenanthroline solution was prepared in a 1 to 1 mixture of ethanol and iron free water. A 0.0334 g portion was dissolved in 50 ml of ethanol and then diluted with 50 ml of water. Any trace (Smith, et al., 1952) of Fe$^{2+}$ in either solvent would produce a red tint in the solution. For extraction of the red ferrous complex, reagent grade isoamyl alcohol was used.

A buffer solution was prepared by dissolving 0.6 moles of Na(OOCCH$_3$) (sodium acetate) in one liter of 0.18 M H$_2$SO$_4$. It was prepared by mixing 600 ml of 1 M Na(OOCCH$_3$) with 360 ml of 0.05 M H$_2$SO$_4$ and diluting to 1 liter. In addition, a solution of 2.0 moles NH$_4$F in one liter of 0.05 M H$_2$SO$_4$ and a saturated solution of EDTA in 0.05 M H$_2$SO$_4$ were prepared.

Experimentally, 5 ml of the ferrioxalate solution was pipetted into a black 30 ml test tube and stoppered in a dark room. Post irradiation processing, also in a dark room, consisted of adding by pipet, 2 ml of the Bph solution, 2 ml of buffer solution and 1 ml of the ammonium fluoride solution. This mixture was shaken and then transferred to a 60 ml separatory funnel to which 5 ml of isoamyl alcohol was added. After shaking, separating, and draining off the aqueous layer, the organic product, which was an emulsion, was transferred to a clear 10 ml test tube. The emulsion was broken by centrifuging at 2000 r.p.m. for
one minute. Finally, the optical density of the organic layer was read on the colorimeter at 533 mµ. The colorimeter was standardized by setting the instrument such that the pure solvent, isoamyl alcohol, registered 100% transmission, i.e., optical density of 0.

Results of the Ferrioxalate Experiments

The first experiments were conducted without using fluoride ions to complex the unreduced ferric ions and Parker's techniques. It was observed that after processing, exposure to normal room illumination caused complete photoreduction and intense coloring regardless of the sample's radiation exposure history. The addition of fluoride during post irradiation processing complexed the unreduced ferric ions forming the very stable FeF₆. To be certain of removing ferric ion from the organic phase and hence to insure the color stability in normal illumination, two 10 ml EDTA wash treatments were given to the alcohol product in the separatory funnel.

Experiments were performed to determine the color stability of samples as a function of ferrous ion concentration. The variables were the pH of the EDTA wash solution, fluoride ion concentration, and combinations of both. In these experiments, the ferrioxalate portion was replaced with equal volumes of a standard ferrous ammonium sulfate solution.

The results of these stability experiments showed that color fading occurred with basic and neutral EDTA washes (Fig. 12). Subsequent experiments revealed that the fluoride addition alone was sufficient for color stability, so the EDTA wash was not necessary.
A calibration experiment was performed to correlate the optical density of the alcohol samples to the amount of ferrous ion present. A group of samples with ferrous iron concentration ranging from $10^{-3}$ M to $10^{-7}$ M were prepared by volumetric dilution of a $2.276 \times 10^{-2}$ M Fe(NH$_4$)$_2$SO$_4$.7H$_2$O solution which was standardized by titrating with ceric ammonium sulfate. These were treated in an identical manner as the ferrioxalate samples and processed in the prescribed manner. Fig. 13 shows the linear relationship between optical densities of colored alcohol solutions with the initial ferrous ion concentration. The effect of fluoride addition on optical density as a function of ferrous ion concentration was negligible as shown in Fig. 14.

The irradiation experiments were performed in radiation environments ranging in dose rates from 10 mr/hr to 10 Kr/hr. It was observed that the system was virtually insensitive below doses of 1 Kr, i.e., there was no noticeable difference in optical density between the irradiated samples and the unirradiated blanks. The results of these experiments are shown in Fig. 15.

Since the maximum dose rate of the Co$^{60}$ irradiation apparatus was only 14.5 mr/hr, this method of irradiation was found to be inadequate and, therefore, was not investigated.

**Experiments With Ferric Bathophenanthroline**

A $10^{-4}$ M solution of ferric sulfate was prepared in 0.12 M HCl by dissolving 0.03 g of A.R. grade Fe$_2$(SO$_4$)$_3$ in one liter of 0.12 M HCl. The pH of this solution was ~2.5.
Fig. 12 The effect of pH on the color density of irradiated ferrioxalate samples when washed with EDTA solutions.
Optical Density

Slope = 69.7

Fe$^{+2}$ concentration in μm/ml x 10$^{-3}$

Fig. 13 The optical densities of ferrioxalate solutions as a function of ferrous iron concentration with bathophenanthroline as an indicator
Fig. 14 The optical density of ferrous Bph solutions as a function of Fe$^{+2}$ concentration after the addition of fluoride ions.
Fig. 15 The optical densities of ferrioxalate-Bph samples as a function of X-ray dose exposure.
The buffer solution for this system was 6.25 M with respect to HCOOH and 3 M with respect to Na(OOCH). It was prepared by mixing 51.01 g of A.R. grade sodium formate with 67.5 ml of 88% HCOOH (formic acid) and diluting to 250 ml. A 0.015 M solution of NaF in 0.12 M HCl was also prepared.

The samples to be irradiated consisted of 2.5 ml of the ferric sulfate solution, 1 ml of the formate-formic acid buffer, and 1.5 ml of the Bph solution in a black test tube. The sample was prepared in the dark, stoppered and shaken. The sealed samples were then irradiated in the accelerator laboratory.

Post irradiation treatment was conducted in a dark room in the following manner: to each sample, 1 ml of 0.015 M NaF was added by pipet. After shaking, the contents of the test tube were transferred to a 60 ml separatory funnel and 5 ml of isoamyl alcohol was then added. After shaking, separating, and discarding the aqueous layer, the organic product was transferred to a clean, 10 ml optically-clear test tube. Again, after centrifuging to separate the emulsion, the optical densities of the samples were measured on the colorimeter.

Results of the Ferric Bathophenanthroline Experiments

From the results of experiments with ferrioxalate, similar experiments were designed to sensitize and stabilize the color in the Fe(Bph) system. The color stability was investigated by experiment using samples which were irradiated to 5 Kr and unirradiated blanks and then treating these with various combinations of fluoride additions and EDTA washings. The results, as shown in Fig. 16, again showed that EDTA was not desirable as a ferric ion complexing agent for this.
An experiment was performed to determine the reproducibility by measuring the color of twelve blank samples. The results showed a ±10% deviation in optical densities. The procedure used was that described in the previous section. This deviation is a measure of the accuracy of the colorimetric determination of ferrous ions by this procedure.

The first experiment to measure optical density as a function of dose was performed by irradiating samples to attain doses of 0.5, 1, 2, and 4 Kr at a dose rate of 5 Kr/hr. The results, as seen in Fig. 17, show a linear relationship with a slope of 0.129 OD/Kr (optical density units/kiloroentgen). The color stability of these samples was good and the optical density did not change over 48 hrs.

In an experiment to determine the effect of dose rate on optical density, samples were irradiated to 2 Kr at dose rates of 2, 5, and 10 Kr/hr. No significant dependence on dose rate was observed. These results are shown in Table I.

Table I

<table>
<thead>
<tr>
<th>OPTICAL DENSITIES OF Fe(Bph) SAMPLES AT VARIOUS DOSE RATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Kr/hr</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>0.69</td>
</tr>
<tr>
<td>0.70</td>
</tr>
<tr>
<td>0.66</td>
</tr>
<tr>
<td>0.72</td>
</tr>
</tbody>
</table>

An attempt to increase the reliability and accuracy of the system was made by premixing the constituents in a larger volume.
(in the dark) with the same proportions described previously. Five ml portions of this mixture were pipetted into each test tube. The deviations in optical densities of identically treated samples were reduced. The results of relatively low level irradiations of solutions prepared in this manner are shown in Fig. 18.

When fresh solutions were prepared with a higher quality (more iron free) distilled water, and the rubber stoppers of the samples were sealed with black tape, a lower background color was observed in the blanks. This allowed more sensitive measurements at low doses and better reproducibility. The results of an irradiation with these conditions are shown in Fig. 19.

The experimental errors attributed to loading, transferring, and processing the chemical dosimeter solutions was initially evidenced in a \( \pm 10\% \) deviation in optical density readings. After many refinements such as premixing constituents, this value was reduced to \( \pm 5\% \). The plot shown in Fig. 20 is a least squares approximation to the data obtained in the three groups of experiments. The range in dose was from 50 r to 2 Kr. All of the data points used were corrected for the optical densities of the blanks. The slope obtained was 0.182 OD/Kr.

The calibration curve for this system was plotted from the results of an experiment similar to that used in the ferrioxalate experiments. Again, a linear plot was obtained with a slope of 74.5 OD/\( \mu \) mole Fe\(^{+2} \) as shown in Fig. 21.

A final question arose about the color stability of irradiated samples with respect to time elapsed between exposure and processing. The results of an experiment in which samples were irradiated to 1 Kr,
showed definite color fading over a period of 40 hr. These results are shown in Fig. 22. This fading is probably due to the reoxidation of the ferrous ions by the oxidants present in the irradiated water solution.
Fig. 16 The optical densities of irradiated ferric Bph samples as a function of time after various treatments of fluoride additions and EDTA washings.
Fig. 17 The optical density of irradiated ferric Bph samples as a function of X-ray dose in the Kr range, using the original procedures.

Slope = 0.129
Fig. 18 The optical density of irradiated ferric Bph sample as a function of X-ray dose in the r range, using the procedure of premixing the reactants.
Fig. 19 The optical density of irradiated ferric Bph samples as a function of X-ray dose in the r range, using the procedure of premixing the reactants and fresh, iron-free solutions.

Slope = 0.189
Fig. 20 A least squares approximation to the data points of four ferric Bph irradiation experiments.

Slope = 0.182
Fig. 21 The optical densities of ferric Bph solutions as a function of Fe$^{+2}$ concentration.

Slope = 74.5
Fig. 22  The optical density of irradiated ferric Bph samples as a function of time between exposure to X-rays and chemical processing.
DISCUSSION

Radiation Mechanisms

The general mechanisms of radiation chemistry include molecular and atomic ionization, formation of excited electronic states, transfer of electronic excitation from one molecule to another, dissociation of excited vibrational states, electron capture, neutralization, and radical reactions (Friedlander and Kennedy, 1960). Molecular excitation accounts for more than half of the energy dissipated by radiation passing through matter.

In these experiments, the X-rays produced have an average energy (≈K longitude) of 59.5 KeV (Fig. 11). At this low energy, the photoelectric effect is the dominant photon interaction (Fig. 23).

![Photoelectric Effect Dominant](image)

**Fig. 23** The relative importance of the three major types of photon interactions. The lines show the values of Z and hν for which the two neighboring effects are just equal. (Evans, 1955)
The photoelectric interaction ejects a bound electron from an atom with an energy \( E = h\nu - B_e \) where \( B_e \) is the atomic binding energy of the electron. This free electron now loses energy through ionizing and radiative collisions in the medium. The electromagnetic radiation produced along the path of a decelerating electron has an intensity proportional to the atomic number of the nuclei in the medium.

The amount of directly excited complex formed is proportional to the amount of radiation absorbed by the complex. The quantity of radiation absorbed by a sample is given by:

\[
I_0 - I = I_0 (1 - e^{-\mu x})
\]

where

\[
\begin{align*}
I_0 &\quad = \text{incident photon intensity} \\
I &\quad = \text{transmitted photon intensity} \\
\mu &\quad = \text{mass absorption coefficient in cm}^{-1} \\
x &\quad = \text{thickness of absorbing medium}
\end{align*}
\]

The variable \( \mu \) is a function of photon energy. For iron, we see in Fig. 24 that much more absorption for direct excitation is due to lower energy photons.

![The total mass absorption coefficient of photons for iron as a function of photon energy (Rockwell, 1954)](image)
The sequence of events involved when a photon is absorbed in water is shown in Fig. 25.

Fig. 25 A schematic representation of the radiation events caused by the absorption of a 59.5 Kev photon in water.

The primary electron has an ionization event every 5000 Å of path length (Allen, 1961). Since the average energy lost by an energetic electron in an ionizing collision with a water molecule is 100 eV, then complete energy dissipation of the electron would produce 600 secondary 100 eV electrons. These secondary electrons, in turn, will ionize H₂O forming radicals and tertiary electrons with an average energy of 20 eV (Field and Franklin, 1957). These species and their respective formation energies are shown in Table II.
Table II

SEVERAL KNOWN ELECTRON-WATER REACTIONS AND THEIR ENERGY REQUIREMENTS

<table>
<thead>
<tr>
<th>Reaction Products</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}^+ + e^-$</td>
<td>12.67 (17)</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{OH} + e^-$</td>
<td>19.6 (18)</td>
</tr>
<tr>
<td>$\text{OH}^+ + e^-$</td>
<td>18.8 (19)</td>
</tr>
<tr>
<td>$\text{O}^+ + \text{H}_2 + e^-$</td>
<td>18.9 (20)</td>
</tr>
<tr>
<td>$\text{O}^+ + \text{H} + \text{H} + e^-$</td>
<td>28.2 (21)</td>
</tr>
<tr>
<td>$\text{H}_2^+ + \text{O} + e^-$</td>
<td>23.1 ± 2 (22)</td>
</tr>
</tbody>
</table>

Thus, every photon absorbed by the solution (20% of the incident flux), produces approximately 3000 electrons, 3000 ions, and 3000 radicals having kinetic energies ranging from thermal to 5 eV.

An Fe$^{+2}$ production balance may be quantitatively expressed using the following facts. In dilute aqueous solutions:

$$1 \text{ rad} = 100 \text{ ergs/cm}^3 = 6.25 \times 10^{13} \text{ eV/cm}^3.$$  

Since the average photon energy is 59.5 Kev;

$$1 \text{ rad} = 1.05 \times 10^9 \text{ photons/cm}^3$$

then, for $\sim$3000 electrons produced per photon:

$$1 \text{ rad} = 3.15 \times 10^{12} \text{ electrons/cm}^3$$

Chemical analysis of a sample exposed to 50 r of X-rays showed an Fe$^{+2}$ concentration of $10^{-7} \text{ M}$ or $6 \times 10^{13}$ atoms/ml. This number compares very well with the theoretical electron yield.
Due to the geometry of the samples and the competing chemical reactions, it can be assumed that the electron mechanism was less than 100% efficient. Other sources of excitation are the excited radicals and ions formed in the solution as seen in Table II. Many secondary electron events with water molecules leave excitation energies in excess of the 4.5 eV required for the $\text{H-O-H} \rightarrow \text{OH} + \text{H}$ reaction.

It may, therefore, be concluded that the difference in the concentration of Fe$^{+2}$ complex measured and that produced directly by the excitation of Fe$^{+3}$ as shown in the mechanisms described on page 8 and Equation 23, is attributed to the indirect excitation of Fe$^{+3}$ by excited molecules, radicals, ions, and electrons which are present in the irradiated aqueous solution. These indirect excitation mechanisms are illustrated by the general type of reactions in Equations (24) through (26) inclusive.

\[
\begin{align*}
\text{Fe}^{+3} + e^- & \rightarrow \text{Fe}^{+2} \quad \text{(direct)} \quad (23) \\
\text{Fe}^{+3} + \text{HCOO}^- + M & \rightarrow \text{Fe}^{+2} + \text{CO}_2 + \text{MH} \quad (24) \\
\text{HOOC}^- + M^* & \rightarrow (\text{HOOC}^-)^* + M \quad (25a) \\
(\text{HOOC}^-)^* + \text{Fe}^{+3} & \rightarrow \text{H} + \text{CO}_2 + \text{Fe}^{+2} \quad (25b) \\
\text{Fe}^{+3} + M^* & \rightarrow \text{Fe}^{+2} + (M^+) \quad (26)
\end{align*}
\]

where M is an active species such as a radical, electron, ion, or molecule which has been excited by the ionizing radiation absorbed by the system, or by the secondary electron interactions.

**Dosimeter Quantum Efficiencies**

In both the ferrioxalate and ferric bathophenanthroline systems,
the main ferric to ferrous conversion deterrent was reoxidation. In the FeBph₃ system, the probability of reoxidation was reduced by the presence of formate ions. The formate ion (Baxendale and Bridge), due to its low ionization energy and high concentration in the dosimeter solution, was a more desirable oxidant than Fe⁺². Other functions of the buffer solution included maintaining a constant pH level during irradiation. The stabilities of virtually all of the complexes were pH sensitive.

The standard measures of chemical efficiency in a chemical dosimeter are the G value and the quantum efficiency (see Appendix). The G value may be calculated (Price, 1952) using an equation which relates energy absorbed by a material to the amount of product formed.

\[
molecules\ product = \frac{9.3 \times 10^4 \ G \times 10^{-2}}{1.6 \times 10^{-12} \times 6.02 \times 10^{23}}
\]

where \(9.3 \times 10^4\) is the energy deposited by 1 Kr of X-rays in aqueous solutions in ergs/g. The G values calculated for the two systems were 0.141 for Fe(Ox)⁺³ and 2.51 for Fe(Bph)⁺³. The Fricke dosimeter had a G value of 15.45. However, the sensitivity of ferrous ion detection with Bph is much greater than the colorimetric detection of ferric ions and, therefore, the Fricke Cell appears to be a less sensitive chemical dosimeter.

The quantum efficiencies were calculated on the basis of 1 rad = 9.85 x 10⁸ photons/cm³ (page 38). The number of Fe⁺² ions detected at 1 Kr for the ferrioxalate system was 1.54 x 10⁻⁴ μm/ml which is
equivalent to $9.24 \times 10^{13}$ Fe$^{+2}$ ions/ml.

$\text{Fe(Ox)}_3^{+3}$ quantum efficiency $\gamma = \frac{9.25 \times 10^{13}}{1.05 \times 10^{12}}$

$\gamma = 87.8$ Fe$^{+2}$ ions/photon

The number of Fe$^{+2}$ ions detected at 1 Kr for the ferric bathophenanthroline system was $2.59 \times 10^{-3}$ μm/ml which is equivalent to $1.56 \times 10^{15}$ Fe$^{+2}$ ions/ml.

$\text{Fe(Bph)}_3^{+3}$ quantum efficiency $\gamma = \frac{1.56 \times 10^{15}}{1.05 \times 10^{12}}$

$\gamma = 1.48 \times 10^{3}$ Fe$^{+2}$ ions/photon

On the basis of G values and quantum efficiencies, the ferric bathophenanthroline system was found to be more sensitive to radiation than the ferrioxalate system.

Conclusions and Recommendations for Future Work

The object of this investigation was to evaluate aqueous solutions of photosensitive ferric compounds as chemical dosimeters. The two systems investigated were exposed to various x and gamma radiation environments. The methods of radiation detection by colorimetric analysis were standardized and optimized.

The following evaluations are based on the calculated results just shown, and the experimental results discussed in Section III. The radiation dose ranges of both systems investigated were relatively high compared to electronic radiation dosimeters. It has been shown that most sensitive results were obtained with the ferric
bathophenanthroline dosimeter. The range of this system was 20 r to 20 Kr. The ferrioxalate system was insensitive below a dose of 1 Kr.

In all chemical dosimetry work, the sensitivity is limited by the method of chemical analysis. Bathophenanthroline is one of the most sensitive iron reagents available. The sensitivity of the colorimetric determinations may be improved by using more effective ferric complexing agents. In a recent work, $Fe^{+2}$ concentration was measured in the presence of $Fe^{+3}$ (Clark, 1962) using bathophenanthroline as an indicator. It was shown that dihydrogen phosphate in a solution pH of 2 to 5 and under a carbon dioxide blanket was a more effective complexing mixture for $Fe^{+2}$ than fluoride or EDTA. The range of detection found was $3.53 \times 10^{-4}$ to 0.053 $\mu$ moles Fe/ml. Maximum color stability was attained by extracting the complex into isoamyl acetate.

Future work using the above mentioned recent improvements should increase the system sensitivity. Another possibility to avoid the peroxide formation would be an iron-organic dosimeter with a low ionization energy. Basic solutions of iron could be attempted using syn-phenyl-2-pyridyl ketoxine (Cluley and Newman, 1963) with EDTA and hydrogen peroxide as color indicators. This combination was not as sensitive as bathophenanthroline for $Fe^{+2}$ determinations. However, there have been no evaluations of the system as a dosimeter.
APPENDIX

The graphical illustrations of the experimental data were mostly linear approximations in accordance to Beer's Law. In Fig. 20, the method of least squares was used to get the best linear approximation to 30 data points. The formulas used in this type of calculation are

\[ n a_1 + \left( \sum_{i=1}^{n} x_i \right) a_2 = \sum_{i=1}^{n} y_i, \]

\[ \left( \sum_{i=1}^{n} x_i \right) a_1 + \left( \sum_{i=1}^{n} x_i^2 \right) a_2 = \sum_{i=1}^{n} x_i y_i, \]

where

- \((x_i, y_i) = i^{th}\) set of \(n\) data points
- \(a_1 = \) the y intercept of the line
- \(a_2 = \) the slope of the line

In Fig. 20, the first point is \((0,0)\) due to the correction of all data to their respective unirradiated blanks; thus, \(a_1 = 0\) and the equations reduce to

\[ a_2 = \frac{\sum_{i=1}^{n} x_i y_i}{\sum_{i=1}^{n} x_i^2} \]

For Fig. 20, \(\sum_{i=1}^{30} x_i^2 = 13,835\) and \(\sum_{i=1}^{n} x_i y_i = 2,517.8\), therefore

\[ a_2 = 0.182. \]
GLOSSARY

A. R.: analytic reagent.

Bph: bathophenanthroline, 4,7-diphenyl-1,10-phenanthroline.

dose: the amount of radiation absorbed by a body.

EDTA: ethylenediaminetetraacetic acid.

G-value: the number of molecules of a material created or destroyed for each 100 eV of energy absorbed.

gram mole (mole): the gram formula weight of a substance expressed in grams.

Molar (M): the number of gram moles of solute in one liter of solution.

(0x)$^{-2}$: oxalate ion

(0x)$^{-}$: oxalate radical ion

Ph: phenanthroline

quantum efficiency (γ): the number of molecules of reactant consumed per quantum of radiation absorbed.

rad: the absorption of 100 ergs of photon energy per gram of material.

roentgen (r): that amount of x or gamma radiation which produces in one cubic centimeter of dry air at standard temperature and pressure, one esu of electricity of either sign. It is also equivalent to the dissipation of 93.7 ergs per gram of water.
LIST OF REFERENCES


Fricke and Morse, Phil. Mag., 7, 129, (1929).


Ibid., 72, 2173, (1950).


