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A Continuous Dosimetry by Use of the Fricke Dosimeter

Ken'ichi SUGIMOTO, Ryuzo TSUJINO and Sōichirō MURAHARA*

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Although the Fricke dosimeter has been commonly used for a standard chemical dosimetry, there still exist real needs for measuring the radiation dose rapidly. In the present work potentiometry was applied to the rapid and continuous measurements of radiation dose using the Fricke dosimeter.

An irradiation vessel equipped with a platinum indicator electrode and a reference electrode (saturated calomel electrode) was used and the potentials of the irradiated ferrous iron solution were measured against the saturated calomel electrode during irradiation. The potential measurements were made at various ferrous iron concentrations and various dose rates. The potential starts from about 380 mV *vs.* S.C.E. and increases gradually with increasing radiation dose until it reaches about 465 mV. The gradient of the potential curve changes with the change of the ferrous iron concentration, but does not change with the change of dose rate. It was found that the potential values observed are in good agreement with the ones calculated from the Nernst equation for ferrous-ferric iron couple in the range of the oxidation ratio from 0.3 to 0.7. As a consequence, the potential *vs.* dose curve can be used for the simple and continuous dosimetry. The error are within 2 per cent at suitable conditions. Good reproducibility over the wide range for the potential measurements is important significance in feature.

1. Introduction

For most purposes of radiation chemistry it is more convenient to compare the amount of chemical reaction in the solution being studied with the amount of change in a standard system, the specific radiation yield of which has been carefully determined by the use of primary physical standards. Various kinds of reaction have been proposed for use as chemical dosimeter¹⁾. Among them, however, only one, that is the oxidation of ferrous iron, has found universal acceptance. The dosimeter using this reaction was first proposed and described in detail by H. Fricke in 1927²⁾ and is called the Fricke dosimeter. In this system, ferrous iron is oxidized to ferric iron in the air-saturated solution of ferrous sulfate in 0.8 *N* sulfuric acid.

Originally Fricke determined the amount of oxidation by titration. Later the amount of ferrous iron disappearing was determined colorimetrically with the use of the *o*-phenanthroline. A notable advance in convenience of use occurred when Hardwick³⁾ pointed out that the quantity of ferric iron formed could be determined very sensitively by direct reading of the optical absorbancy of the solution with an ultraviolet spectrophotometer at the wavelength 305 m μ . At this wavelength the light absorption of ferric iron in sulfuric acid has a maximum, while the absorption of ferrous iron is negligible.

For most radiation-chemical work, the Fricke dosimeter will remain the chief standard for a long time to come. However, it has the disadvantage that the analytical procedure

* Department of Applied Chemistry, College of Engineering.

requires considerable time. Therefore, rapid determination of ferric iron formed is most required. In the present paper a zero current potentiometry was applied to the simple continuous dosimetry⁴⁻⁵).

2. Experimental

Irradiations.—The γ -radiation was provided by a 100 curie cobalt-60 source⁶). The rate of energy absorption was determined by the rate of ferrous oxidation in an aerated 0.8 *N* sulfuric acid solution assuming that 15.60 ferrous ions are oxidized per 100 eV of absorbed energy⁷). Initial dose rate values for the source are shown in Table 1. All the irradiations were carried out at ambient temperature of about 10°C.

A vessel containing ferrous iron solution was equipped with a platinum electrode, a saturated calomel electrode, and a salt bridge. The vessel was placed in the irradiation chamber. The electrodes were connected through the lead wires with a potentiometer placed on the outside of the irradiation chamber and the oxidation-reduction potentials of ferrous-ferric iron couple were measured periodically during the irradiations.

Table 1. Distribution of dose rate in the irradiation facilities.

| Position | Irradiation distance cm | Dose rate $\times 10^4$ r/hr | Intensity $\times 10^{19}$ eV/l/min |
|----------|----------------------------|---------------------------------|--|
| 1 | 3.48 | 9.72 | 9.4 |
| 2 | 4.48 | 5.86 | 5.7 |
| 3 | 5.48 | 3.93 | 3.8 |
| 4 | 6.48 | 2.86 | 2.8 |
| 7 | 9.48 | 1.59 | 1.5 |

Preparation of solutions.—All solutions used for irradiations were prepared from specially purified water which was obtained by distilling ordinary redistilled water before use. The chemicals, reagent grade ferrous ammonium sulfate and sulfuric acid, were used without further purification. Stock solution of ferrous iron was prepared by dissolving reagent grade ferrous ammonium sulfate in sulfuric acid solution and diluting with water to the final desired concentration for both ferrous iron and acid.

Procedure.—In a Pyrex irradiation vessel 10 ml of ferrous ammonium sulfate solution was taken. This solution was saturated with air by bubbling a vigorous stream of clear air for 30 minutes just before each irradiation. The air was purified by passing it through a glass filter and then bubbling it through distilled water. Finally, the platinum electrode was dipped into the solution, and this half cell was connected with the saturated calomel electrode through the salt bridge. The solution was then irradiated and the measurement was made as follows.

Oxidation-reduction potential measurements.—The yield of ferric iron was determined by oxidation-reduction potential. All potential measurements were made at about 10°C using Shimadzu potentiometer 3P.

3. Results and Discussion

The effects of irradiation time, dose rate and initial concentration of ferrous ammonium sulfate on the oxidation-reduction potential were investigated.

Effect of irradiation time.—In Fig. 1 the oxidation-reduction potentials are plotted against irradiation time at the dose rate 9.72×10^4 r/hr. The potential curve starts at about 380 mV vs. S.C.E., then increases with increasing irradiation time and finally approaches approximately 465 mV. This curve fits close to the curve calculated on the basis of the Nernst equation except for the initial and final parts. Curve A in Fig. 2 shows a relation between oxidation-reduction potential and oxidation ratio of iron. This curve was obtained from the twelve potential curves at various concentrations of ferrous iron and dose rates. While, curve B was obtained from the Nernst equation taking the formal potential of ferrous-ferric iron couple in 0.8 *N* sulfuric acid as 0.67 V. As is shown in Fig. 2, the potentials in the range of the oxidation ratio between 0.3 and 0.7 apparently indicate oxidation-reduction potential of ferrous-ferric iron couple. In this case, oxidation ratio of iron indicates the ratio of ferric iron formed by irradiation to total iron.

During irradiation there appeared no singularity on the oxidation-reduction potential. It appeared that the measurements have no effect on the potential of saturated calomel electrode. However, a difference of two potential curves in Fig. 2 appeared at the extreme values of oxidation ratio. At these portions the potentials measured are probably those of the other systems, that is, the system involving dissolved oxygen at the portion of extremely small oxidation ratio and that involving hydrogen peroxide generated from water radiolysis at the portion of large oxidation ratio. The radiation dose required for complete oxidation of ferrous iron is somewhat less than that which shows constant potential.

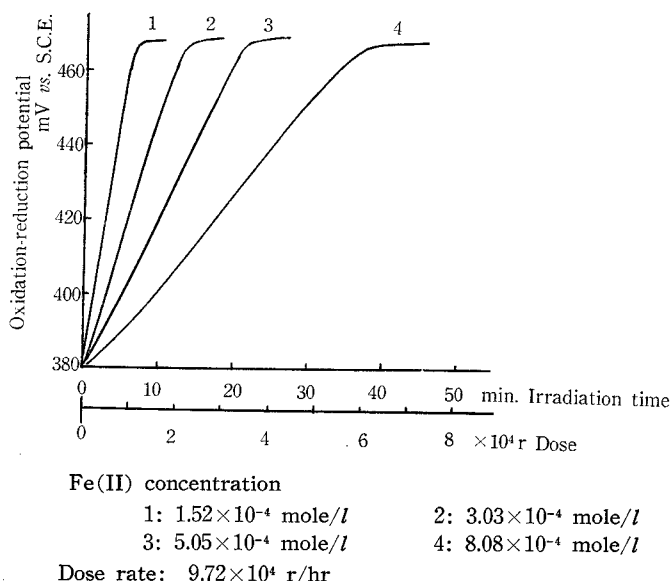


Fig. 1. Oxidation-reduction potential vs. dose curves on various ferrous concentrations.

Effect of radiation dose rate.—The dose rate was varied to determine this effect. Fig. 3 shows the potential against radiation dose on various dose rate values. Three curves in Fig. 3 coincide with one another within experimental error. From these results, it can be seen that the potential curve is essentially independent of dose rate.

Effect of initial ferrous iron concentration.—To determine the effect of the initial concentration of ferrous iron, various solutions were prepared for irradiation. The results of measurement with these solutions are shown in Fig. 1. The gradient of potential curve decreases with increasing initial concentration of ferrous iron. The radiation dose which shows constant potential corresponds to the ferrous iron concentration. Consequently, in the continuous dosimetry low concentration of ferrous iron is required for lower dose measurement and high concentration for higher dose.

Reproducibility of the potential curve.—As is shown in Tables 2, 3 and 4 the measurements of the oxidation-reduction potential are highly reproducible and the most reproducible results are obtained at the potential from 400 mV to 450 mV. These results suggest that potentiometry for acidic ferrous ammonium sulfate solution can be used as a continuous dosimetry of γ -ray irradiation. A large variability at small oxidation ratio is probably due to the potential variation of dissolved oxygen as a function of hydrogen ion concentration.

Continuous dosimetry.—Ferrous ammonium sulfate is the most useful compound for practical dosimetry because of the ease of handling, sensitivity, precision and relative stability. The range of total dose in which the Fricke dosimeter is useful is limited by

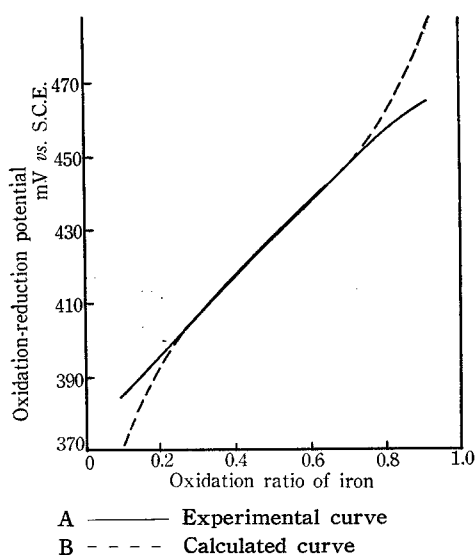


Fig. 2. Oxidation-reduction *vs.* oxidation ratio of iron curves: Experimental curve and calculated curve.

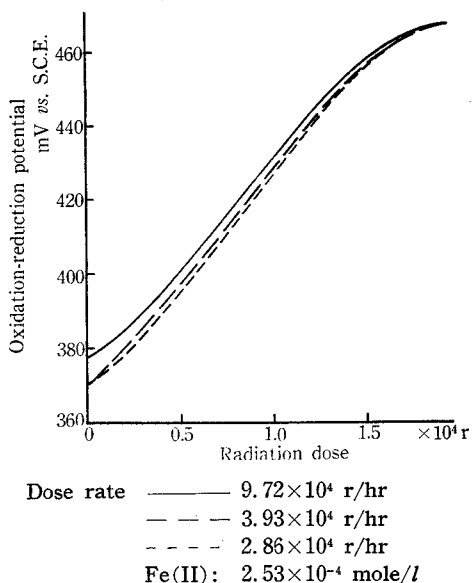


Fig. 3. Oxidation-reduction potential *vs.* dose curves on various dose rate.

the consumption of dissolved oxygen. In air-saturated solutions oxygen is used up by a dose of about 40,000 r. The useful range can be extended about fivefold by saturating the solution with pure oxygen. The precision of dose measurement is risen by the suitable choice of the ferrous iron concentration, because the oxidation-reduction potential depends on the ratio of ferrous to ferric iron.

Table 2. Reproducibility of the oxidation-reduction potential curves.

Dose rate: 9.72×10^4 r/hr Fe(II): 3.03×10^{-4} mole/l

| Total dose $\times 10^4$ r | Oxidation-reduction potential mV vs. S.C.E. | | | | Reproducibility % Average error |
|-------------------------------|--|-------|-------|---------|---------------------------------------|
| | 1 | 2 | 3 | Average | |
| 0.00 | 380.0 | 389.1 | 380.0 | 383.0 | 1.07 |
| 0.21 | 383.8 | 393.0 | 386.7 | 387.8 | 0.89 |
| 0.42 | 395.5 | 402.0 | 401.3 | 399.6 | 0.68 |
| 0.63 | 405.5 | 407.2 | 409.7 | 407.5 | 0.36 |
| 0.84 | 413.7 | 415.2 | 419.6 | 416.2 | 0.55 |
| 1.05 | 425.0 | 425.0 | 429.0 | 426.3 | 0.42 |
| 1.26 | 432.7 | 432.0 | 436.0 | 433.6 | 0.37 |
| 1.47 | 443.7 | 439.3 | 444.0 | 442.3 | 0.45 |
| 1.68 | 450.0 | 446.8 | 453.7 | 450.2 | 0.53 |
| 1.89 | 456.9 | 455.2 | 460.8 | 457.6 | 0.46 |
| 2.10 | 462.3 | 461.0 | 465.0 | 462.8 | 0.32 |
| 2.31 | 463.3 | 464.5 | 468.6 | 465.5 | 0.45 |
| 2.52 | 463.3 | 464.9 | 468.8 | 465.7 | 0.45 |
| 2.73 | 463.3 | 466.7 | 468.8 | 466.3 | 0.42 |

Table 3. Reproducibility of the oxidation-reduction potential curves.

Dose rate: 9.72×10^4 r/hr Fe(II): 5.05×10^{-4} mole/l

| Total dose $\times 10^4$ r | Oxidation-reduction potential mV vs. S.C.E. | | | | Reproducibility % Average error |
|-------------------------------|--|-------|-------|---------|---------------------------------------|
| | 1 | 2 | 3 | Average | |
| 0.00 | 369.3 | 353.0 | 369.2 | 363.8 | 2.00 |
| 0.24 | 375.3 | 365.7 | 380.5 | 373.8 | 1.45 |
| 0.48 | 386.8 | 377.3 | 389.9 | 384.7 | 1.27 |
| 0.72 | 392.4 | 383.4 | 398.3 | 391.4 | 1.36 |
| 0.96 | 399.7 | 395.2 | 404.3 | 399.7 | 0.76 |
| 1.20 | 408.0 | 405.3 | 413.2 | 408.8 | 0.70 |
| 1.44 | 416.5 | 413.5 | 419.2 | 416.4 | 0.46 |
| 1.68 | 422.7 | 422.5 | 424.9 | 423.4 | 0.24 |
| 1.92 | 427.7 | 428.8 | 430.6 | 429.0 | 0.24 |
| 2.16 | 432.7 | 437.5 | 436.2 | 435.5 | 0.42 |
| 2.40 | 440.3 | 442.8 | 446.3 | 443.1 | 0.47 |
| 2.64 | 448.8 | 452.7 | 451.6 | 451.0 | 0.33 |
| 2.88 | 453.5 | 459.7 | 457.7 | 457.0 | 0.50 |
| 3.12 | 460.9 | 465.2 | 468.2 | 464.8 | 0.55 |
| 3.36 | 465.2 | 469.0 | 473.7 | 469.3 | 0.62 |
| 3.60 | 469.5 | 472.7 | 473.7 | 472.0 | 0.35 |
| 3.84 | 469.5 | 472.7 | 473.7 | 472.0 | 0.35 |

Table 4. Reproducibility of the oxidation-reduction potential curves.

Dose rate: 3.93×10^4 r/hr Fe(II): 2.53×10^{-4} mole/l

| Total dose $\times 10^4$ r | Oxidation-reduction potential mV vs. S.C.E. | | | | Reproducibility % Average error |
|-------------------------------|--|-------|-------|---------|---------------------------------------|
| | 1 | 2 | 3 | Average | |
| 0.10 | 357.5 | 356.3 | 357.5 | 357.1 | 0.15 |
| 0.20 | 357.5 | 354.8 | 363.4 | 358.6 | 0.90 |
| 0.30 | 363.7 | 361.6 | 369.0 | 364.8 | 0.77 |
| 0.40 | 368.3 | 374.7 | 379.4 | 374.1 | 1.04 |
| 0.50 | 375.8 | 379.3 | 385.0 | 381.7 | 1.02 |
| 0.60 | 384.0 | 385.2 | 390.0 | 386.4 | 0.62 |
| 0.70 | 391.7 | 391.0 | 396.7 | 393.1 | 0.60 |
| 0.80 | 400.0 | 398.0 | 402.2 | 400.1 | 0.36 |
| 0.90 | 406.0 | 406.4 | 408.7 | 407.0 | 0.27 |
| 1.00 | 410.0 | 413.3 | 412.6 | 412.0 | 0.32 |
| 1.10 | 414.7 | 419.7 | 415.8 | 416.7 | 0.47 |
| 1.20 | 421.0 | 424.4 | 421.3 | 422.2 | 0.35 |
| 1.30 | 426.1 | 430.0 | 426.8 | 427.6 | 0.37 |
| 1.40 | 432.7 | 436.8 | 431.5 | 433.7 | 0.48 |
| 1.50 | 439.2 | 445.2 | 436.8 | 440.4 | 0.73 |
| 1.60 | 443.7 | 453.0 | 441.0 | 445.9 | 1.06 |
| 1.70 | 447.0 | 462.8 | 446.0 | 451.9 | 1.61 |
| 1.80 | 451.5 | 464.3 | 449.6 | 455.1 | 1.34 |
| 1.90 | 456.3 | 465.8 | 454.8 | 459.0 | 0.99 |
| 2.00 | 459.3 | 467.3 | 456.7 | 461.1 | 0.90 |

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