P
The Ferrous Sulfate Radiation Dosimeter
A Calorimetric Calibration with Gamma Rays^{*†}
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The ferrous sulfate radiation dosimeter (herein called the Fricke dosimeter) has been recalibrated by a calorimetric method in which assumptions regarding energy absorbed in the glass and the heat capacity of the calorimeter have been eliminated. The 100 ev yield, $G(Fe^{++} \rightarrow Fe^{+++})$, is 15.8 ± 0.3 for Co^{60} gamma radiation in agreement with the Hochanadel-Ghormley value. The result is compared with other G values obtained by other methods and it is recommended that the low value be adopted for Co^{60} gamma radiation and for electrons in the 1-2 Mev range.

The oxidation of ferrous sulfate in 0.8N sulfuric acid solution by ionizing radiations¹ satisfies most of the requirements of an aqueous dosimeter.²

¹ Hereafter referred to as the "Fricke dosimeter," this system was first investigated by H. Fricke and S. Morse, Amer. J. Roent. Radium Therapy 18, 430 (1927); Phil. Mag. 7, 129 (1929).

² N. Miller and J. Wilkinson, Faraday Soc. Disc. 12, 50 (1952).

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Unfortunately general adoption of this system is prevented by serious discrepancies in the 100 ev yield³ reported by different authors (Table I).

³The 100 ev yield, $G \equiv G(Fe^{++} \rightarrow Fe^{+++})$, is defined as number of Fe^{2+} ions oxidized, or Fe^{3+} ions produced, per 100 ev absorbed in the solution.

The reasons for these discrepancies⁴⁻¹⁰ have not heretofore been under-

⁴N. Miller, J. Chem. Phys. 18, 79 (1950).

⁵T.J. Hardwick, Can. J. Chem. 30, 17, 39 (1952).

⁶C.J. Hochanadel and J.A. Ghormley, J. Chem. Phys. 21, 880 (1953).

⁷R.W. Hummel, Ph.D. Thesis, University of Saskatchewan, 1953; cf. R.W. Hummel, A.B. Van Cleave and J.W.T. Spinks, Can. J. Chem. 31, 1203 (1953).

⁸S. Davison, S.A. Goldblith, B.E. Proctor, M. Karel, B. Kan and C.J. Bates, Nucleonics 11, No. 7, 22 (1953).

⁹C.B. Amphlett, Faraday Society Disc. 12, 272 (1952).

¹⁰J. Saldick and A.O. Allen, private communication.

stood. Suggested explanations have included (i) dose rate dependence at high dose rates, (ii) organic impurities in the dosimeter solution and (iii) errors in absolute measurement of the energy absorbed. The recent work of Miller¹¹ has shown

¹¹N. Miller, Nature 171, 688 (1953).

that the oxidation yield is independent of dose rate up to 100,000 r/min, provided the solution contains dissolved oxygen. Therefore, unless the solution becomes oxygen-depleted, dose-rate dependence cannot be considered a serious source of error. In aerated solutions many organic impurities enhance the oxidation

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TABLE I. Calibration of Fricke dosimeter

3.

Ionization method			
Authority	Radiation	<u>G</u>	
Fricke and Morse ¹	X-rays	18.0	
Miller ⁴	Ra γ -rays	19.9	
	1.2 Mv X-rays	21.1+ <u>1.3</u>	
Hardwick ⁵	Co ⁶⁰ γ -rays	20.4+ <u>0.3</u>	
	P ³² β^-	21.1+ <u>0.5</u>	
	S ³⁵ β^-	20.2+ <u>0.9</u>	
Hochanadel and Ghormley ⁶	Co ⁶⁰ γ -rays	16.7	
Hummel ⁷	Ra γ -rays	15.2	
	24.5 Mv X-rays	15.5+ <u>0.4</u> or 15.9+ <u>0.4</u>	
	Co ⁶⁰ γ -rays	15.8+ <u>0.2</u>	
Calorimetric method			
Authority	Radiation	<u>G</u>	
Hochanadel and Ghormley ⁶	Co ⁶⁰ γ	15.6+ <u>0.3</u>	
Davison et al. ⁸	Co ⁶⁰ γ	20.2	
Hardwick ⁵	P ³² β^-	21.1+ <u>0.5</u>	
Power input method			
Authority	Electron energy Mev	Beam current μ mamps	<u>G</u>
Amphlett ⁹	0.92	0.001	17
Hochanadel and Ghormley ⁶	1.33	0.065-1.5	16.8
Davison et al. ⁸	3.0	not given	$\sim$ 20
Jaldick and Allen ¹⁰	1-2	6x10 ⁻⁵ -0.5	15.6+ <u>0.5</u>

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yield.¹² Their presence can be ascertained by the addition of sodium chloride to

¹²H.A. Dewhurst, Trans. Faraday Soc. 48, 905 (1952).

the dosimeter solution.¹² This technique was recently applied by Hart¹³ in a re-

¹³E.J. Hart, private communication

determination of the absolute yield with tritium-beta particles. He found that addition of sodium chloride decreased the yield from 15.5 to 12.8. Hochanadel and Ghormley⁶ reported that with polystyrene irradiation cells the oxidation yield depended on the time the solution was in contact with the cell. They suggest that the higher yields obtained with polystyrene cells at low dose rates may result from dissolved organic matter. Miller¹⁴ has recently found that on prolonged

¹⁴N. Miller, private communication.

irradiation (> 24 hours) in the presence of lucite the oxidation yield increased about 5%; this increase was eliminated by addition of sodium chloride. In agreement with his previous observations, and contrary to Hochanadel and Ghormley, Miller² found that polystyrene had no effect on the oxidation yield. Perhaps, the disagreement is to be attributed to differences in the polystyrene samples used. Large errors, which are difficult to detect, may occur in the absolute determination of the absorbed energy. The techniques usually employed for evaluation of the energy absorbed are (i) ionization chamber measurement, (ii) power input (i.e. current and voltage) measurement of a low-current electron beam and (iii) calorimetric measurement.

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The absolute oxidation yields given in Table I are summarized according to the method used to evaluate the energy absorbed. The ionization chamber G values vary over such a wide range that establishment of a most probable value on such basis is impossible. The power-input measurements tend to favor a relatively low value for the yield. The calorimetric data give values at both extremes and nothing between. Because of the convenience and extensive use of the Fricke dosimeter the importance of establishment of the absolute yield is evident. In this laboratory we have repeated and extended the calorimetric calibration of this dosimeter both for selection of a most probable G value and for comprehension of the discrepancy in the heretofore reported calorimetric measurements.

2. EXPERIMENTAL

2.1 Materials

All solutions were prepared with triply distilled water; i.e., laboratory distilled water further purified by distillation from acid dichromate and then from alkaline permanganate in an all-pyrex apparatus.

Baker's CP analyzed ferrous ammonium sulfate was used without further purification. It has been reported that recrystallization does not affect the yield.⁶ Known amounts of the ferrous ammonium sulfate were dissolved in the purified water made 0.8N in sulfuric acid (Bakers CP analyzed reagent). Concentration of ferrous ion ranged from 5×10^{-4} M to 10^{-3} M. Addition of 10^{-3} M sodium chloride (Merck reagent) to these solutions did not change the yield.

2.2 Analytical Method

Amount of ferric ion produced was determined spectrophotometrically by its own absorption in 0.8N H_2SO_4 at 305 m μ using a Beckman model DU spectro-

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photometer equipped with thermostated hydrogen lamp. Optical density measurements (in 1.0 cm silica cells) were made at a temperature of $22.5 \pm 0.1^\circ\text{C}$ approximately one-half hour after irradiation. This method requires accurate control of the solution temperature because the measured extinction coefficient increases about 0.8% per degree C. Separate determination of the decadic molar extinction coefficient yielded a value of 2160 ± 10 liters mole⁻¹ cm⁻¹ at 22.5°C .

2.3 Apparatus

An approximately 300 curie cobalt-60 source similar to that described by Hochanadel and Ghormley¹⁵ was used. The experimental arrangement, shown

¹⁵C.J. Hochanadel and J.A. Ghormley, Rev. Sci. Inst. 22, 473 (1951).

in Figure 1, consisted of a brass source positioner (for ensurance of reproducible geometry), cavity heater and adiabatic calorimeter. The cavity heater was made of nichrome ribbon wound on a triangular framework which almost completely filled the cavity; its function was to maintain the temperature of the calorimeter surroundings equal to that of the water in the calorimeter bulb. The adiabatic calorimeter consisted of a cylindrical brass jacket on the exterior surface of which an insulated nichrome heater was wound and on the interior of which was located a pyrex bulb containing a water sample. The space between jacket and bulb was continuously evacuated with a mechanical pump during a calibration.

To ensure uniform wall thickness calorimeter bulbs were made on a glass lathe. The size of each suitable bulb was modified to obtain desired glass fraction and volume. During use the calorimeter bulb was sealed at the neck (through which all electric connections to the water were made) with a droplet of apiezon wax.

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Temperatures of water, calorimeter jacket and cavity were measured with copper-constantan thermocouples with the reference junctions at 0°C. A Rubicon high precision potentiometer (No. 40077) in conjunction with a Rubicon spotlight galvanometer of 0.0012 microampere/mm sensitivity was used for measurement of thermocouple potential differences. To facilitate the temperature balance readings the thermocouple circuit was arranged so that the voltage outputs were in opposition with a resultant zero deflection when the temperatures were equal. All temperatures were read to the nearest half microvolt.

For electrical calibration a small resistance heater with copper leads was totally immersed in the water. A 6-volt heavy duty storage battery continuously charged through a constant voltage transformer supplied current to the heater. Through suitably arranged precision resistors (calibrated against a Wheatstone bridge in turn calibrated against Bureau of Standards calibrated resistors) it was possible to obtain with a single reading on a Rubicon precision potentiometer a voltage corresponding to both the current through the heater and voltage across it.¹⁶ The heating time was recorded with an electrical timer actuated by a

¹⁶W.P. White, Modern Calorimeter, The Chemical Catalog Co. p. 134 (1928).

relay switch connected to the heating circuit.

2.4 Calorimetric Method

The adiabatic calorimetric method is particularly suited to the measurement of the very small temperature rise caused by absorption of γ -ray energy. These measurements are necessarily of long duration and it is essential therefore that thermometric and calorimetric errors be accurately known or entirely

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eliminated. Such errors were eliminated by the method of comparative measurements¹⁷ employing electrical calibration.

¹⁷W. Swietoslawski, Microcalorimetry, Reinhold Publishing Corp., 1946.

The calorimeter was calibrated electrically by measurement of temperature rise as a function of time at constant rate of energy input. From the relation energy input = $\underline{EIt} = \underline{E^2t/R}$ joules, the energy equivalent of the calorimeter was obtained from the equation

$$\frac{\Delta \underline{Q}}{\Delta \underline{t}} = \frac{\Delta \underline{T}}{\Delta \underline{t}} \cdot \underline{H_c} \quad (1)$$

where $\Delta \underline{Q}/\Delta \underline{t}$ is the rate of electrical energy input in ev/min, $\Delta \underline{T}/\Delta \underline{t}$ the measured rate of temperature rise in microvolts/min, and $\underline{H_c}$ the energy equivalent of the calorimeter in ev/microvolt. The rate of γ -ray energy absorption by the calorimeter, $(\Delta \underline{Q}/\Delta \underline{t})_\gamma$, was then calculated from the following equation,

$$\left(\frac{\Delta \underline{Q}}{\Delta \underline{t}} \right)_\gamma = \underline{H_c} \left(\frac{\Delta \underline{T}}{\Delta \underline{t}} \right)_\gamma \quad (2)$$

To determine the amount of γ -ray energy absorbed by the ferrous sulfate solution it was necessary to correct for (i) energy absorbed by the glass and (ii) energy absorbed in 0.8N sulfuric acid. The correction for (i) was made empirically (see section 3.2) and for (ii) it was assumed that the energy absorbed in 0.8N sulfuric acid was greater than that in water by the ratio of their densities; i.e., 1.025.

All γ -ray measurements were made inside the cylindrical cobalt source (Figure 1). Prior to the temperature measurements the water samples were irradiated for sixteen hours. This ensured that steady state Concentrations of decomposition products (H_2 , H_2O_2 , O_2) were attained, thus eliminating any error

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due to heat of chemical reaction. The temperature of the water was recorded every ten minutes for a period of one to three hours. In every case the temperature-time plots were linear.

In this type of source an effort is made to have a nearly homogeneous gamma-radiation field in the region of exposure but it is known, from experiment, that such an objective is not achieved. To satisfy the question whether local inhomogeneities in the field might affect the G values, calorimetric calibrations were performed in various positions with the smallest volume calorimeter bulb. The G values so obtained did not vary by more than experimental error.

3. CALIBRATION OF DOSIMETER

The calibration of the Fricke dosimeter by Hochanadel and Ghormley was based on a calculated heat capacity for the calorimeter and on the assumption that the amount of energy absorbed by the glass was proportional to its weight fraction. Neither of these assumptions is necessary for interpretation of the data herein reported.

3.1 Effect of Cavity Heating

For reconciliation of the results of Hochanadel and Ghormley and of Davison et al. it was necessary to study the effect of cavity heating on the calorimetric measurements. The former authors used a cavity heater to obtain adiabatic conditions whereas the latter used a heater wound directly on the calorimeter jacket.

In these experiments energy was introduced by electrical heating at known and constant rate into a calorimeter bulb of known weight containing a known weight of water. Temperature rise per unit energy input was studied as a function of rate of energy input. In every case linear temperature-time plots were

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obtained. The results are summarized in Table II. With cavity heating the calibration, expressed as the ratio microvolts temperature rise per joule input, remained essentially constant whereas in the absence of cavity heating (jacket heating only) the ratio increased slowly with increased rate of energy input. It is noteworthy that at the highest rate of energy input in absence of cavity heating the ratio became equal to that with cavity heating, while at the low rate, comparable to the γ -ray heating rate, the ratio was about 35% lower. The conclusion was that with jacket heating only, heat leakage would be an important consideration in our experiments.

TABLE II. Effect of Cavity Heating.

Weight of water = 7.103 g; weight of glass = 1.418 g.

Energy input, joules/min	Cavity heating		Absence of cavity heating	
	Heating rate, volts/min	Calibration, volts/joule	Heating rate, volts/min	Calibration, volts/joule
0.193	0.258	1.337	0.188	0.974
0.979	1.301	1.328	1.034	1.056
1.922	2.545	1.324	2.250	1.171
3.309	4.375	1.322	4.150	1.254
5.275	7.000	1.327	6.850	1.298
8.468	11.23	1.326	11.22	1.325

Because of space limitations Davison et al. were forced to use a jacket heater which covered the wall and bottom of the calorimeter jacket. The top of calorimeter their/was not heated and the possibility of heat leakage should be considered. Such an effect may account in part for the high yield obtained by these authors. However the jacket heating they employed was probably more efficient than that used in our

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experiments because both top and bottom of our calorimeter were unheated.

In some of our early experiments we calibrated electrically at a heating rate corresponding to the gamma-ray heating rate. Under such conditions the $\underline{G}$ values established were in good agreement with those obtained using cavity heating. In the experiments used as a basis for the results here reported (i.e., in what we consider our most reliable work) we used a combination of both cavity and jacket heating.

3.2 Glass Fraction Correction

The correction for energy absorbed by the glass was made by varying the ^{weight} glass weight-fraction at constant volume and extrapolating to zero glass/fraction. A typical example is shown in Table III. $\underline{G}$ (apparent) was calculated from the total energy absorbed in the calorimeter and includes the density correction. Table III contains the pertinent data from which $\underline{G}$ (apparent) was calculated. These results were analyzed by the method of least squares which gave the equation,

$$\underline{G}(\text{apparent}) = 15.8 \pm 0.3 - (15.5 \pm 0.3) \underline{W}_g \quad (3_{11})$$

where $\underline{W}_g$ is the glass weight fraction and the subscript in (3_{11}) refers to the volume of solution in ml. Equation (3_{11}) gives experimental confirmation to the assumption made by Hochanadel and Ghormley that the amount of energy absorbed in the glass is proportional to its weight fraction.

The results obtained at several volumes are presented in Figure 2, which shows $\underline{G}$ (apparent) as a function of the glass weight-fraction. The individual groups of points are expressed by equation (3_{11}) and the following equations

$$\underline{G}(\text{apparent}) = 15.7 \pm 0.3 - (16.1 \pm 0.5) \underline{W}_g \quad (3_4)$$

$$\underline{G}(\text{apparent}) = 15.8 \pm 0.3 - (15.4 \pm 0.3) \underline{W}_g \quad (3_7)$$

$$\underline{G}(\text{apparent}) = 15.8 \pm 0.3 - (15.8 \pm 0.3) \underline{W}_g \quad (3_{15})$$

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TABLE III. Correction for glass fraction.

Weight water, Grams	Glass fraction	Calibration, $10^{18}\text{ev}/\mu\text{volt}$	δ -heating, $\mu\text{volt}/\text{min}$	δ -energy, $10^{18}\text{ev}/\text{cc-min}$	Fe^{2+} oxidized, $10^{15}\text{ ions}/\text{cc-min}$	$\underline{G}(\text{apparent})$
10.99	0.320	10.8	0.383	3.76	41.8	10.8
11.02	0.220	7.40	0.467	3.14	39.8	12.4
11.25	0.156	10.5	0.317	2.96	40.7	13.4
10.90	0.121	7.13	0.426	2.79	39.7	13.9
11.14	0.059	9.84	0.299	2.64	40.3	14.9
Graphical Extrapolation						15.8

Within the precision of the work the yield is independent of the volume with an extrapolated value 15.8 ± 0.3 in agreement with the calorimetric measurements of Hochanadel and Ghormley and the ionization chamber measurements of Hummel.

3.3 Evaluation of Errors

An analysis was made of the errors involved in the electrical calibration measurements, the γ -ray energy determinations and the chemical measurements. The precision of the electrical calibration measurements was 0.4% of which 0.2% was instrumental and 0.2% was attributed to the resistors in the heater circuit. A precision of 0.3% for the temperature measurements was obtained from a least-squares analysis of a typical set of temperature-time results. The total error in the determination of the absolute amount of γ -ray energy absorbed was $\pm 0.7\%$. The chemical measurements had a precision of 1.2% which resulted from a contribution of 0.5% from uncertainty in the extinction coefficient and 0.7% from range of reproducibility of a series of chemical irradiations. The evaluation of the errors therefore puts a limit of $\pm 1.9\%$ on the precision of the G values reported.

4. Conclusion

Although the calorimetric method of absolute energy determination is essentially sound and should provide a reliable technique for dosimeter calibration, precaution must be taken to avoid uncompensated heat losses.

Of the determinations of G for the Fricke dosimeter heretofore made in this way, only the Hochanadel-Ghormley Co⁶⁰ work appears to adopt adequate precautions against such loss and is thus considered inherently more reliable.

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This view is strengthened by the nature of the agreement shown in Table I, namely with the more recent Co^{60} results of Hummel, who used ionization chamber technique, and with those of Saldick and Allen, who used the power-input method for 1-2 Mv electrons from a Van de Graaff generator.

In the Hochanadel-Ghormley determinations assumptions were made in regard to glass-fraction correction and heat capacity of the system. In the determination herein reported, these assumptions were eliminated. The values respectively $\underline{G} = 15.6 \pm 0.3$ and $\underline{G} = 15.8 \pm 0.3$, are within the limits of error the same as the Hummel value 15.8 ± 0.2 and the Saldick-Allen value 15.6 ± 0.5 .

On the basis of these results it may be unqualifiedly concluded that the low $\underline{G}$ value for the Fricke dosimeter is correct.

The authors express their appreciation to Dr. C.J. Hochanadel, Dr. J.A. Ghormley, Mr. A. Kuppermann and Dr. R.W. Hummel for many valuable discussions.

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Figure 1. Layout of calorimeter in Co^{60} source. Legend:
A, cavity heater; B, calibration heating filament; C, water thermocouple; D, jacket heater; E, cavity thermocouple; F, jacket thermocouple; G, cobalt in wall of brass cylinder; H, to vacuum system; I, brass source positioner.

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Figure 2. $\bar{G}$ (apparent) as a function of glass weight-fraction in the calorimeter for calorimeter bulbs of different volume. Legend: ○ 4 ml; ● 7 ml; ⊙ 11 ml; ⊗ 15 ml.

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1. The invention relates to a method of determining the weight of a substance in a container, the substance being of a material having a known specific gravity, and the container being of a material having a known weight.