Chemical Dosimetry of Gamma Rays, Neutrons and Accelerated Electrons

Cemil B. ŞENVAR

Department of Physical Chemistry, Faculty of Science, University of Ankara

Özet : Son yıllarda büyük bir hızla gelişmekte olan kimyasal dozimetre sistemlerinden biri olan *«Fricke Dozimetresi»* ile *Gama ışınları, termik nötronlar* ve *hızlı elektronların* dozimetrisi yapıldı. Dozimetre çözeltisine Cl^- iyonlarının müsbet tesiri incelendi ve tadil edilmiş çözeltilerle çalışarak :

(a) Argonne millî laboratuvarındaki 0,5 ilâ 1700 curie'lik beş muhtelif Co - 60 kaynağının belli uzaklıklarda verdikleri γ dozları;

(b) Van de Graaff makinesinin verdiği 0,3 ve 1,0 MeV enerjili elektronların verdiği doz mikdarları; ve

(c) (CP - 5) reaktörünün termik kolonundaki termik nötron akısı tayin edildi.

Bulunan neticelerin diğer metodlarla yapılan tayinleri desteklediği ve tadil edilmiş Fricke Dozimetresinin belli bir doz sınırı içinde olmak şartiyle güvenilir neticeler verdiği kanaatine varıldı.

* * *

The standard Fricke Dosimeter (1) (2) is used in determining the dose rates obtaided from various sources of radiation, i.e. gamma rays from Co-60 sources, accelerated electrons from Van de Graaff machine and mixed (thermal neutrons + gamma) fluxes in the thermal column of Argonne's CP-5 reactor.

When aerated ferrous sulfate solution is irradiated with X-rays, γ-rays, α particles, electrons, etc., first water decomposes(3) to give free radicals (H, OH) and molecular products(H_2, H_2O_2) :

$$H_2O + \text{Radiation} = H,\ OH,\ H_2,\ H_2O_2 \qquad (1)$$

Then the following series of reactions occur :

$$OH + Fe^{++} = Fe^{+++} + OH^- \qquad (2)$$

$$H + O_2 = HO_2 \qquad (3)$$

$$H_2O_2 + Fe^{++} = Fe^{+++} + OH^- + OH \quad (4)$$

$$HO_2 + H^+ + Fe^{++} = Fe^{+++} + H_2O_2 \quad (5)$$

$$HO_2 + Fe^{+++} = Fe^{++} + O_2 + H^+ \quad (6)$$

The last reaction does not occur if the concentration of sulfuric acid is high, i.e., 0,8 N.

According to the above scheme each H atoms (radical) leads, through formation of HO_2, to the oxidation of three Fe^{++} ions; each ·OH radical oxidizes one, and each H_2O_2 oxidizes two Fe^{++} ions. The Ferric yield for this system is 15,6 (*).

It has been suggested recently that sodium chloride should be used to suppress the effect of organic impurities in the solution, because in general organic impurities tend to increase the Fe^{++} oxidation rate as follows(4): In the irradiation of the dosimetric solution in presence of O_2 and organic compounds (RH), such as formic acid, free radicals produced from water react in the following way

$$HCOOH + OH = H_2O + HCOO \quad (7)$$

$$HCOO + O_2 = HO_2 + CO_2 \quad (8)$$

$$HO_2 + H^+ = H_2O_2 \quad (9)$$

$$Fe^{++} + H_2O_2 = Fe^{+++} + OH^- + OH \quad (10)$$

If chloride is present in sufficient concentration the organic substance cannot react as above, and the chloride ion exerts a sort of protective effect, due to the following reactions:

$$OH + Cl^- = Cl + OH^- \quad (11)$$

$$Fe^{++} + Cl = Fe^{+++} + Cl^- \quad (12)$$

The latter two reactions are able to compete for OH radicals. However Cl^- ion does not inhibit the effect of unsaturated organic materials, but most organic impurities are of the saturated type. (5)

Experimental results show that in general the yield of molecular products (G_{H_2} and $G_{H_2O_2}$) increases and the yield of free radicals (G_H and G_{OH}) decreases with increasing density of ionization. (6, 7)

(*) Ferric yield $G_{Fe^{+++}}$ is defined as : Number of Fe^{++} ions converted to Fe^{+++} ions per 100 ev energy absorbed.

This means that, if we have α particles or $B^{10}(n, \alpha)$ Li^7 recoil products (high ionization density) we have mostly molecular products in solution, and as only H_2O_2 çan cause oxidation, the total ferric yield wil be small; while in the case of γ-rays the opposite happens and there will be mostly free radicals present in the solution beside H_2O_2 which eventually leads to higher oxidation rates (higher yields). When the particle causes high iozation density along its track (as with α particles), the free radicals H and OH can recombine easily giving the molecular products H_2 and H_2O_2. When the ionization density is low (γ-rays, X-rays, electrons) the free radicals can escape recombination and cause more oxidation of ferrous to ferric.

The ferric yields of various types of radiation and nuclear particles with standard ferrous dosimeter are given in Table 1.(8, 9)

Table 1.

Source of Radiation or Reaction	Radiation or Nuclear Particle	Energy Mev	Oxygenated Fricke Dosimeter, $G_{Fe^{+++}}$ (molecules/100 ev)
Co^{60}	γ-rays	1.25	15.6 ± 0.3
—	X-rays, elektrons	—	15.6
$H^3 \rightarrow He^3$	β^-	0.00569	12.9 ± 0.2
$Po^{210} \rightarrow Pb^{206}$...	α	5.3	6.2 ± 0.2
$B^{10}(n, \alpha)Li^7$Recoils	α Li^7	1.50 0.85	4.4
Li^6 (n. α) H^3...	α H^3	2.05 2.73	5.2 ± 0.5

Experimental

(a) For the determination of γ dosages from a number of Co—60 sources, pyrex glass irradiation cells of ~ 12 cc capacity and at least 8 mm internal diameter are used. The furnace treated cells are filled with ferrous sulfate dosimeter solution and irradiated for a certain time at a certain distance from the source and the ferric ion concentration formed is measured with a spectrophotometer at 3020 A°. The molar extinction coefficient is found to be $\varepsilon = 2228$ as shown in Figure 1.

For γ-rays, X-rays and electrons the dose rate is calculated from the following relations:

$$\text{Dose Rate in (ev/l min)} = \left(\frac{6.023 \times 10^{17} \times 100}{15.6}\right) \cdot a$$

where $a = \mu\text{N}$ ferric produced per minute;

Or:

$$(r/\text{min} = \left(\frac{6.023 \times 10^{17} \times 100 \times 1.602 \times 10^{-12}}{1000 \times 15.6 \times 93}\right) \cdot a$$

Or:

$$(\text{Rads/min}) = (r/\text{min}) \times 0.93$$

(b) For mixed thermal neutron and gamma flux measurements, four different solutions are prepared, one containing no Boric acid and the other three being 10,20 and 30 mM in Boric acid respectively. Silica radiation cells of $\sim$ 12 cc capacity are filled with the solution and 16 of them are placed in a cardboard box in random Latin Square pattern.(11) The box is irradiated 46 $^1/_2$ inches in from the face of thermal column of CP—5 for 7.5 minutes. This time is measured from the time full power (2 MW) is reached until the reactor is scrammed. The reactor is brought up on a 42 second period. The solutions are analyzed for ferric by spectrophotometer. The standard deviation in ferric concentration is calculated and found to be 13 micronormal. The gamma flux is calculated from the ferric concentration of the solution without Boric acid.

As the ferric yield ($G_{Fe^{+++}}$) for B^{10} (n, α) Li^7 reaction is 4.4 (Table 1), the following equations (10) are used

$$dN/dt = G_i \, (dE_i/dt)$$

$$(dN/dt)_{Fe^{+3}/l\ \text{sec}} = 4.4 \, (dE_n/dt)_{100\ \text{ev}/l\ \text{sec}}$$

where dN/dt is the number of ferric ions formed per liter per second, and dE_n/dt is the energy liberated in units of 100 ev per B^{10} (n, α) Li^7 reaction. On the other hand $(dE_n/dt)_{100\ \text{ev}/l\ \text{sec}}$ can be expressed in terms of known constants:

$$(dE_n/dt)_{100\ \text{ev}/l\ \text{sec}} = (E_r/100\ \text{ev}) \times \phi \times \sigma \times M \times 6.023 \times 10^{23} = k\,\phi$$

where $E_r = 2.34$ Mev per B^{10} disintegration ; ϕ = neutron flux (n/cm^2 sec), σ = Cross section of Boron $= 737\times10^{-24}$ cm^2 and M = Concentration of Boric acid (moles/l).

The constant k is then given by

$$k = (2.34\times10^4)\times737\times10^{-24}\times6.023\times10^{23}\,\text{N} = 1.03\times10^7\times\text{M}$$

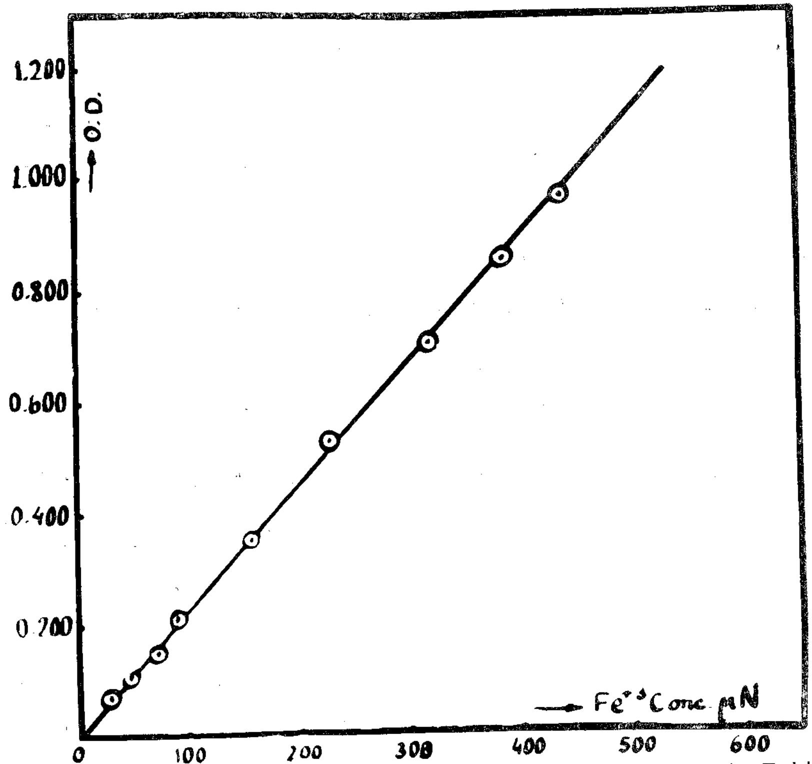

Fig. 1. Determination of molar extinction coefficient (ε) for Fe^{++}—Fe^{+++} system ; t = 28°C ; λ = 302 mμ ; ε = 2228.

and

$$(d\text{N}/dt)_{\text{Fe}^{+3}/l\ \text{sec}} = 4.4\times k\times\phi = 4.53\times10^7\times\text{M}\times\phi$$

from which ϕ is calculated.

(c) For dosimetry of 1 Mev and 0.3 Mev electrons from the Van de Graaff accelerator, the machine is first calibrated by using ferrous dosimetry. By irradiating ~ 5 ml ferrous dosimetric solutions in special cylindrical glass cells, covered with very thin mica sheets, the dose rates under stirred and unstirred conditions are determined. The dose rates of solutions which are not stirred but kept on a moving miniature train are also determined.

When the relationship between the oxidation rates for the three cases, i.e., stirred, unstirred and "on the train„ are established a number of rats and mice which are fixed on the train, together with dosimeter solutions are irradiated for a certain time; The solutions are analyzed in the spectrophotometer and dosages acquired by the animals (wich are irradiated by the Biology department) are calculated. The length of circular train track is 484 cm, the diameter of the electron beam is 1.5 cm and the animals as well as the ferrous solutions passed under the electron beam once every 10 seconds. In calculating the doses, the ferric yield for the solutions which are on the train are multiplied by the ratio of oxidation (stirred/train).

The doses given to the animals are calculated in Rads/min and in (Rad. g/cm².Mev):

$$\text{Dose in (Rad g/cm}^2\text{.Mev)} = \mu\text{ eq. Fe}^{+++} \times 0.349 \times 10^5$$

where $$0.349 \times 10^5 = \frac{6.023 \times 10^{17} \times 100 \times 1.602 \times 10^{-12}}{15.6 \times 100 \times 1.77}$$

(1.77 is the surface area of the electron bean in cm²).

Results

Calibration of Co-60 sources

Five laboratory Co-60 sources (0.5 to ∼ 1700 curies) are calibrated using ferrous sulfate dosimeter. The dosage rates obtained are shown in Table 2.

The dose rate values obtained are plotted on the calibration chart for these sources which was started in 1952. The results in Table 2 which are obtained between the 9 th and 21 st of November 1956, are in good agreement with the results of previous workers, showing also that the geometry of the chambers have not changed since then.

Table 2
Calibration of Co—60 sources

Source number	Approx. Curies	Dose Rates					
		At 3 cm distance		6 cm		9 cm	
		10^{19} ev/l min	r/min	10^{19} ev/l min	r/min	10^{19} ev/l min	r/min
A—1	0.5	0.0447	7.7	0.0117	2.0	0.0054	0.93
H—3	5	0.433	74.5	0.146	25.1	0.0682	11.7
H—1	11	1.010	174.0	0.330	56.8	0.156	26.8
H—4	30	2.610	398 0	0.870	150.0	0.420	72.2
I —1	1685	147.2	25300	—	—	—	—

Effect of Organic Materials on Ferrous Sulfate Dosimeter

The effect of formic acid as an organic impurity on the ferrous sulfate dosimeter is investigated by making up solutions of 1 mN ferrous sulfate, 0.8 N sulfuric acid in triply distilled water and adding formic acid to make the solutions 0.01, 0.1, 1 and 5 mN with respect to the formic acid. The compensating effect of sodium chloride is investigated by using solutions of 1 mN ferrous sulfate, 1 mN formic acid in 0.8 N sulfuric acid made 0.01, 0.1, 1 and 5 mN with respect to sodium chloride.

These solutions together with blank 1 mN ferrous sulfate in sulfuric acid, are irradiated with one of the Co—60 sources (H—1 at 3 cm distance). The results are plotted in Figures 2 and 3. The addition of 0.01 mN and 0.1 mN formic acid has no influence on the Fe^{+++} yield. 1 mN and 5 mN formic acid however have an appreciable effect (Figure 2). Addition of sodium chloride less than 1 mN does not change the yield appreciably, but 1 mN and 5 mN sodium chloride brings back the ferric yield to its normal value (Figure 3).

These results show the reason for using sodium chloride at a certain concentration with the Fricke dosimeter.

An additional set of experiments is carried out using the standard ferrous dosimetric solution and arbitrary amounts of

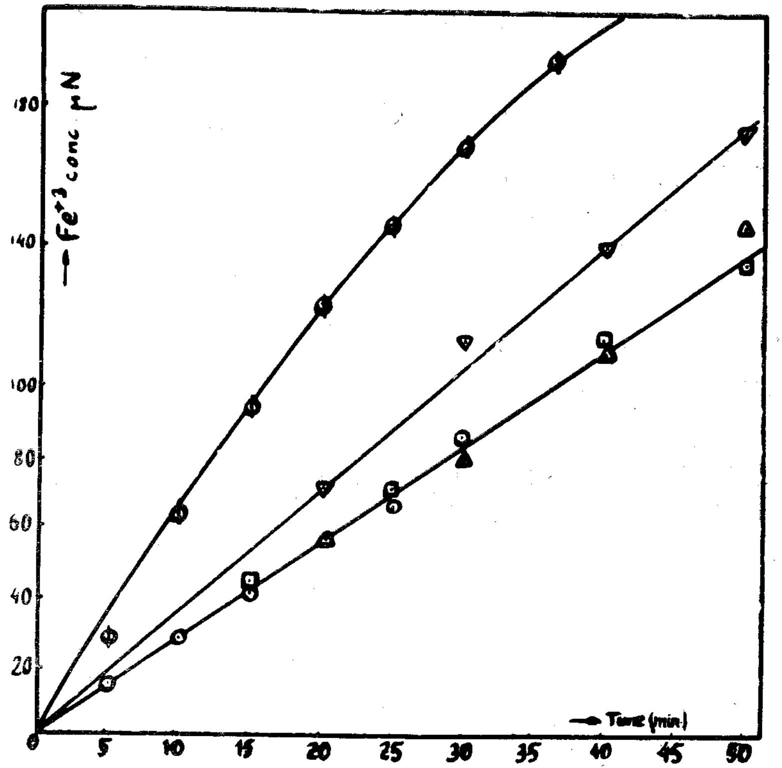

Fig. 2. Effect of formic acid on ferrous oxidation rate. ⊙ 1 mN $FeSO_4$; ⊡ 1 mN $FeSO_4$ + 0,0106 mN HCOOH; △ 1 mN $FeSO_4$ + 0.106 mN HCOOH; ▽ 1mN $FeSO_4$ + 1.06mN HCOOH; Φ 1 mN $FeSO_4$ + 5.31 mN HCOOH

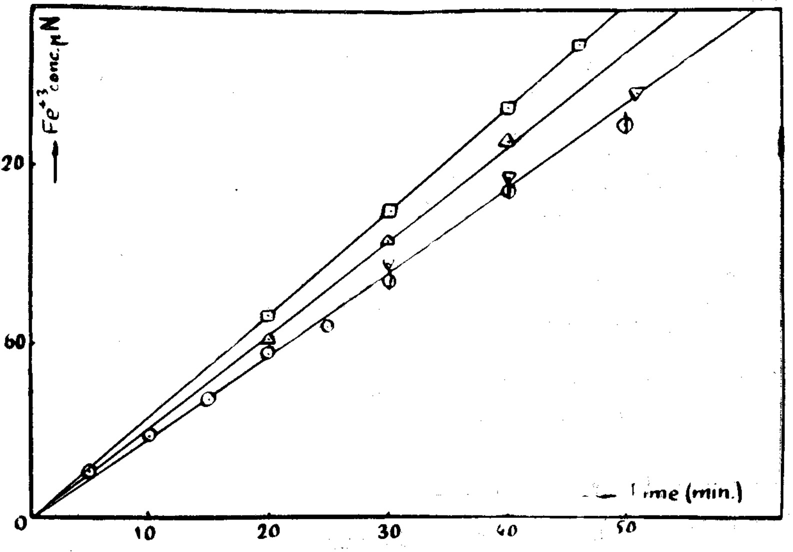

Fig. 8. The Compensating effect of sodium chloride on ferrous dosimetric solutions.

⊙ 1 mN FeSO; ⊡ 1 mN $FeSO_4$ + 1 mN HCOOH + 0,01 mN NaCl;
△ 1 mN $FeSO_4$ + 1 mN HCOOH + 0,1 mN NaCl;
▽ 1 mN $FeSO_4$ + 1 mN HCOOH + 1mN NaCl;
Φ 1 mN $FeSO_4$ + 1 mN HCOOH + 5 mN NaCl.

dust (from laboratory benches) being added to it purposely. The results indicate that dust causes a decrease in ferric yield and thouroughly cleaned (preferably furnace treated) irradiation cells should be used in dosimetry.

Neutron Flux Measurements

The results for the neutron and gamma flux measurement at one location in the thermal column of the CP-5 reactor, are shown in Table 3 and plotted in Figure 4.

Table 3.

	Solution 1	Solution 2	Solution 3	Solution 4
Concentration of Boric acid (mM) . . . . :	0	10	20	30
Total ferric production (μN) . . . . :	104	168	228	276
Total ferric production (10^{18} ions/l min) . . . :	8.3	13.47	18.27	21.25
Total ferric production (μN/min). . . . . :	13.79	22.40	30.40	35.40
Ferric formed from gamma's (10^{18} ions /l min)	8.3	8.3	8.3	8.3
Ferric formed from(B^{10},n) reaction (10^{18} ions/ l min). . . . . :	0	5.17	9.97	12.95
Gamma flux (r/min). . :	918			
Thermal neutron flux (n/cm² sec). . . . . . . :	1.76×10^{11}			

These values are compared in Figure 5 with those obtained at a later date by another worker.(*)

Accelerated Electron Dosimetry

The ratio of oxidation in the solutions which were stirred to the one which were on the train is found to be 1.14 for 1

(*) Thanks are due to Mr. J. T. Harlan Jr. for permission to use his unpublished results.

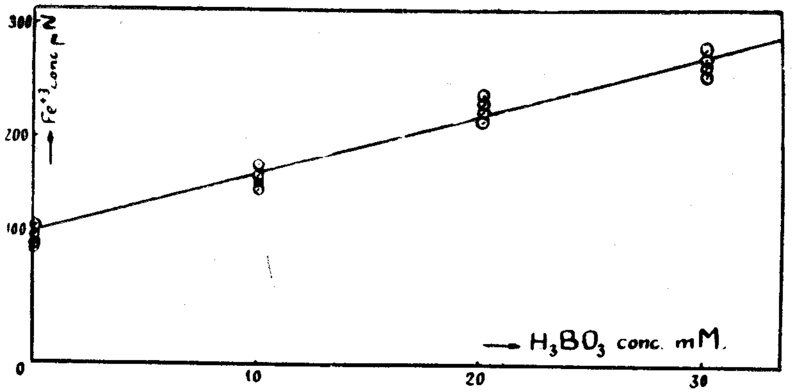

Fig. 4. Ferric production as a function of Boric acid concentration in Thermal column of CP-5. Irradiation time : 7,5 minutes. Solution 46 $\frac{1}{2}''$ in from the face of thermal column. Gamma flux = 918 r/min ; $\Phi_{th}=1,76\times10^{11}$ n/cm^2 sec.

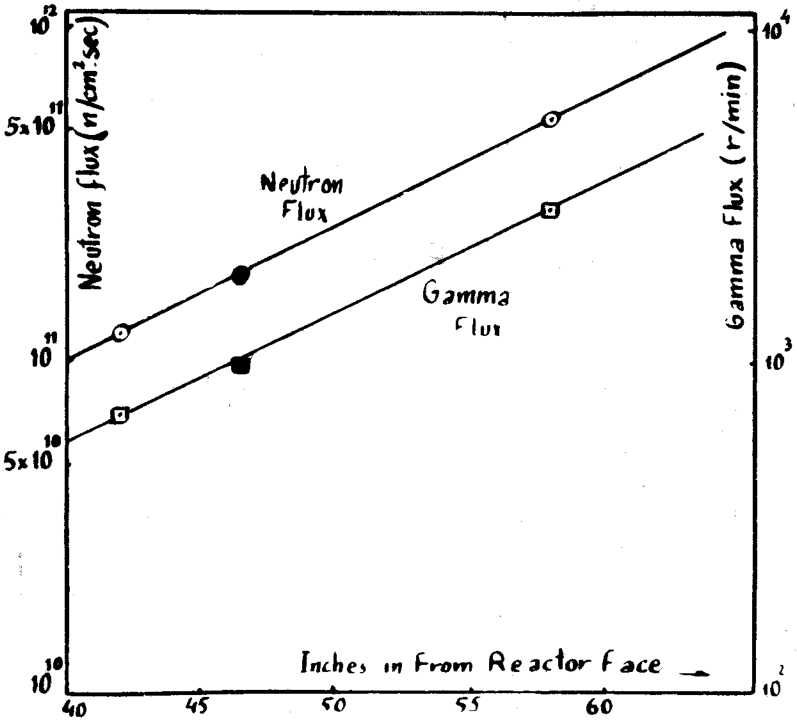

Fig. 5. Comparison of neutron and gamma fluxes on CP - 5 thermal column.

●, ■ This work

⊙, ⊡ J. T. Harlans's results.

Mev electrons, and 1.26 for 0.3 Mev. Some of the experimental results are shown in Table 4, where H means high speed stirring, L low speed stirring, R and M refer to irradiated rats and mice respectively, T means "on the moving train without stirring„ and *m* is minute. The ratio of ferric yield (μ *eq*/min) of stirred to unstirred is between 2 and 3. The speed of stirring does not have an appreciable effect on the ferric production rate.

The rats were given ∼ 7500 (Rads *g*/cm² Mev) and the mice ∼ 3750 (Rads *g*/cm² Mev).

Table 4

Energy of electrons (Mev)	Stirring	Irradiation time	Target current (μ a)	Ferrous liquide volume (cc)	Ferric formed (μ eq/min)	Dose: (Rads g per cm² per MeV)	Dose rate: Rad/min
1.0	Yes	15 sec	0.06	4.72	7.56	—	98800
1.0	No	30 »	0.06	4.78	3.12	—	40300
1.0	No	9mT	0.06	4.72	0.0206	7400	270
1.0	No	»	0.06	4.78	0.0212	7600	272
1.0	No	»	0.06	4.72	0 0191	6850	252 R
1.0	No	»	0.06	4.85	0.0206	7360	264 R
1.0	No	»	0.06	4.72	0.0224	8000	293 R
1.0	No	»	0.06	4.85	0.0196	7000	252 R
1.0	No	4.5mT	0.06	4.79	0.0212	3800	281 M
1.0	No	»	0.07	4.79	0.0206	3580	265 M
0.3	No	9mT	0.14	4.79	0.00538	7100	70 R
0.3	No	»	0.16	4.79	0.00528	6950	68 R
1.0	Yes (H)	15 sec	0.049	4.82	4.40	—	—
1.0	Yes (L)	»	0.049	4.72	4.62	—	—
0.3	No	20mT	0.16	4.84	0.0012	—	—
0.3	Yes	1 m	0.14	4.72	0.488	—	—

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