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Chemical Dosimetry of Pulsed Electronic Radiation

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Existing methods for chemical dosimetry of pulsed electronic radiation are reviewed. Sources of this type of radiation are described, and the special problems arising in the dosimetry of high dose rates (up to 10^{14} rad s^{-1}) are discussed. The effect of dose rate on the yield of radiolysis products is discussed in detail for a number of systems used in dosimetry (aqueous solutions, organic liquids, polymers, gases, etc.). Dosimetric systems particularly suitable for different ranges of dose rate are listed. 112 references.

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1. INTRODUCTION

Pulsed electronic radiation, generated by electron accelerators, has become widely used in radiation chemistry during the last few decades. This development arose, in the first instance, as a result of the penetration of pulse radiolysis into radiation-chemical practice. A powerful, short pulse of high-energy electrons can generate short-lived particles (free radicals, ions, excited molecules) in quantities sufficient to allow their detection by existing physicochemical methods. This enables the particles to be identified and their reaction kinetics to be measured directly. The method has been discussed in monographs [1,2] and in review articles [3,4], and it has given results of fundamental significance in radiation chemistry and in many other fields of science (chemical kinetics, photochemistry, radio-biology, etc.).

A system subjected to a pulse of this type receives a fairly high dose (up to 10^6–10^7 rad). The pulse is of very short duration (usually 10^{-6}–10^{-9} s). Hence, radiolysis by pulsed radiation usually involves very high dose rates (up to 10^{13}–10^{14} rad s^{-1}), which give rise to a number of special features in the radiolytic reactions induced in the system. For example, competitive reactions of the radical–solute and radical–radical type become important in aqueous systems (see Ref. 1). This is an additional reason for the growing popularity of pulsed electron radiation among research workers.

Lastly, electron accelerators are already fairly widely used in radiation chemistry (see, for example, Ref. 5). Hence, accelerators capable of generating pulsed radiation are also likely to find applications.

Obviously, correct dosimetry of pulsed radiation is one of the main prerequisites to the successful application of this type of radiation in radiation-chemical experiments. The recent literature contains a large number of papers on the chemical dosimetry of pulsed radiation. The earlier work is discussed in recent books [1,2] and in a recent review [6]. The present review deals with results published up to the middle of 1971.

2. SOURCES OF PULSED ELECTRONIC RADIATION

Pulsed electronic radiation is usually generated with linear accelerators. These machines can produce either trains of pulses with a prescribed periodicity or single pulses. Pulses of electrons can be obtained also in accelerators of other types with special attachments. In recent years, pulse accelerators of the "Febetron" type, operating on the capacitor discharge principle, have become popular in radiation chemistry laboratories outside the Soviet Union. They are the most powerful accelerators yet developed, giving electron pulses corresponding to currents of thousands of amperes. Other accelerators capable of producing pulsed electron radiation include the dynamitrons and resonance transformers. The operating characteristics of typical sources of pulsed electron radiation are listed in Table 1.

The length of the pulses produced by linear electron accelerators is usually of the order of 10^{-6}–10^{-9} s. However, these pulses usually have a fine structure. For example, a single pulse from the Vickers accelerator at Toronto University, 3.5×10^{-8} s long, actually consists of approximately 100 pulses 2×10^{-11} s long separated by 3×10^{-10} s intervals [13]. The linear accelerator installed at the Argonne National Laboratory (USA) has very similar characteristics: the fine structure of the pulses generated by this accelerator [14] is shown in Fig. 1. Thus, modern electron accelerators offer pulses as short as $\sim 10^{-11}$ s to the research worker.

Pulsed electron accelerators can be used also to generate pulses of X-rays by focussing the electron beam from the accelerator on a heavy-metal target (tungsten, lead, gold, etc.). The method has been used to measure the radiation-induced electrical conductivity of various liquids [21-23].

Table 1. Characteristics of pulsed electron accelerators.

Type of accelerator	Electron energy, MeV	Pulse length, μs	Maximum pulse current, A	References
"Metropolitan Vickers" linear accelerator	1.8	2	0.5	7
"Associated Electrical Industries" linear accelerator	4	0.2 or 2	0.1	8
"Applied Radiation Corporation" linear accelerator	13	0.4—5	0.15	9
"Varian Associates" linear accelerator	7	1.5—5	0.18	10
Ditto	4	0.006—0.05	0.5	11
	4	1.6	0.32	
"U-12" linear accelerator	4—5	2—3	0.1—0.2	12
"Vickers Engineering" linear accelerator	48	0.035	1.0	13
	48	$2 \cdot 10^{-5}$	~15	
	11	0.5—10	2.5	14
"Applied Radiation Corporation" linear accelerator	19—21	0.01	20	
"Febetron 705" (Field Emission Corporation) accelerator	2	0.05	$5 \cdot 10^3$	15
"Febetron 706" (Field Emission Corporation) accelerator	0.5—0.6	0.003	up to ~10^4	16
Cockroft-Walton accelerator	0.8—1.2	0.6 and 5	0.8	17, 18
	3	0.001—0.1	5	19
"High Voltage Engineering" Van de Graaf accelerator	3	5	1	
"Mitsubishi" Van de Graaf accelerator	3	0.3—3.5	0.2	20

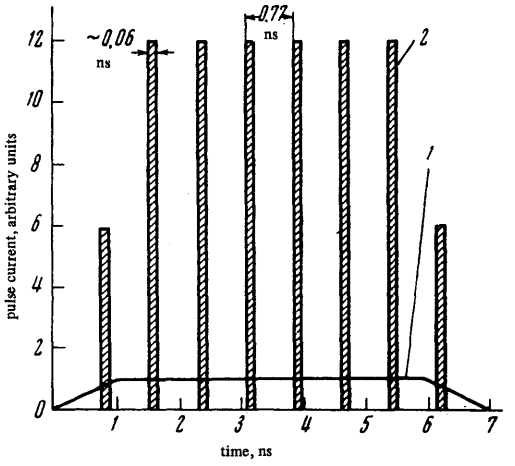


Figure 1. Fine structure of the electron pulses generated by the "Applied Radiation Corporation" (USA) linear accelerator: *1*) macro-pulse, *2*) individual micro-pulse.

3. GENERAL COMMENTS

A knowledge of the following basic parameters is needed in radiation-chemical experiments with pulsed radiation: the dose per pulse absorbed by the system, the pulse length, and the pulse waveform. As an example, oscillograms of the electron pulses generated by various accelerators are shown in Fig. 2.

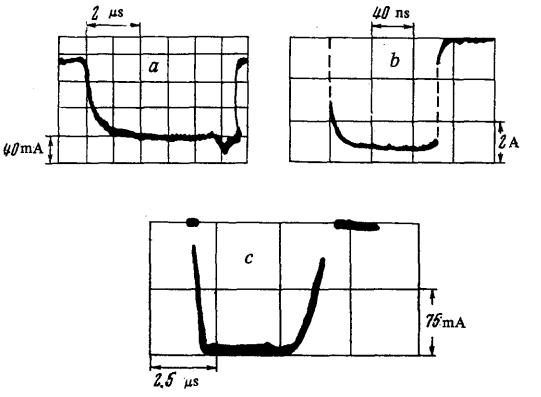


Figure 2. Oscillographic traces of electron pulses generated by (*a*) a linear accelerator [9], (*b*) a Van de Graaf accelerator [19], (*c*) a Cockroft–Walton accelerator [17].

If the duration of the pulse is $\leqslant 10^{-6}$ s the resulting, short-lived radiolysis products have half-lives greatly in excess of the pulse length. The reactions involving these products take place, effectively, after the pulse has subsided. Hence, in these reactions the dose per pulse (which determines the concentration of short-lived products) is more important than the dose rate (which determines the rate of formation of these products). The dose per pulse is measured by physical or by chemical methods. Among the former, calorimetric methods are the most important [19,24-26]. Willis and coworkers [19,26] used an aluminium disk as the calorimeter. With liquid samples, the calorimetric disk was identical in shape and size to the volume of the experimental liquid [26]. However, the method does not lend itself to studies of radiolysis in gaseous systems. In this case, thin disks covering a range of thickness are used, and the dose in an infinitely thin calorimeter is found by extrapolation to zero thickness [19]. Ionisation methods are not suitable for dose measurements in pulsed radiation experiments because the intensities are too high [27,28]. If the average energy of the electrons in the irradiated system is known, the dose can be found by measuring the charge in the system (if sufficiently conducting) [1,17]. The charge can be conveniently measured with an integrator based on capacitor discharge.

In the vast majority of radiation-chemical experiments, doses have been measured by chemical methods. The dose is calculated from the amount of chemical reaction induced by the radiation in some suitably chosen system. Chemical dosimetry has been discussed in recent monographs [29,30] and reviews [6].

Two types of dosimetric measurement are used in pulse radiolysis, depending on the aim of the experiment. If the experiment is designed to measure the radiation-chemical yield of a specific product, we need to know the mean dose over the whole sample volume. If, on the other

hand, we are monitoring short-lived particles by some optical method we need to know the optical density of the system as well as the dose. In this case, since the dose field is never uniform within the cell, one measures the dose absorbed along the path of the monitoring light beam rather than over the whole of the sample.

At the very high dose rates produced by pulsed electron radiation the radiation-chemical yields of many dosimetric systems differ from the values measured at less extreme dose rates. In aqueous dosimetric systems the effect is due to recombination of the primary radiolysis products of water (hydrated electrons e^-_{aq}., hydrogen atoms, OH radicals). Evidently, we must allow for this effect when using aqueous systems for the dosimetry of pulsed radiation.

Many authors have reported a characteristic change in the yield of the radiation-chemical changes of practically all dosimeters based on aqueous solutions. The recombination of the primary radiolysis products of water can be inhibited by using relatively high concentrations of solutes.

The yields under pulsed radiation conditions can also be different (as compared, for example, with γ-radiolysis) in gaseous dosimeters. The effect has been reported, in particular, in mixtures of oxygen and nitrous oxide (see Section 9).

Electron accelerators are complex machines whose operation presents a number of special problems. Although the current does not usually vary by more than 10% from pulse to pulse, much larger variations are occassionally produced. A significant shift in the position of the beam is also possible. These effects can lead to large experimental errors: in order to ensure against these errors it is desirable to monitor the dose rate continuously throughout the experiment. Various methods have been used for this purpose. Keene[8,31] has monitored the electron beam with a secondary emission ionisation chamber, in which the electrons pass through a thin metal foil in a vacuum before reaching the sample cell. Slow secondary electrons appear at the surface of the foil, giving a charge which is proportional to the number of incident fast electrons[8,31-33]. The chamber can be calibrated, for example, against the ferrous sulphate dosimetric system. Schmidt and Buck[34] monitored the dose by bringing the beam to rest in a copper target situated behind the sample cell and measuring the charge acquired by the target. Other methods of monitoring the dose rate have also been described[1,35-37]. In linear accelerators a change in beam current usually gives rise to a significant change in electron energy. Gass and coworkers[38] have described a novel magnetic analyser for measuring electron energies, which can be located within the accelerator in front of the exit window.

4. THE FERROUS SULPHATE DOSIMETRIC SYSTEM

The ferrous sulphate system, usually called the Fricke dosimeter, is most commonly used in radiation chemistry to measure dose. The dosimeter consists of a 10^{-3} M solution of Fe^{2+} in 0.4 M H_2SO_4, saturated with air and containing 10^{-3} mole litre^{-1} of NaCl. Irradiation causes oxidation of bivalent to tervalent iron, with a $G(Fe^{3+})$ value of 15.6 ions/100 eV for solutions of this composition at low dose rates.

Many workers[17,18,24,39-50] find that $G(Fe^{3+})$ for the Fricke dosimeter begins to decrease at dose rates of $\sim 10^8$ rad s^{-1}. The decrease is found[40,44,47] to be even greater when the solution contains NaCl. However $G(Fe^{3+})$ can be made practically independent of dose rate up to $\sim 6 \times 10^9$ rad s^{-1} by increasing the concentration of Fe^{2+} ions to 10^{-2} M and saturating the solution with oxygen[42,44,47-49]. $G(Fe^{3+})$ is 16.07 ions/100 eV for the γ-radiolysis of a solution of this composition[48]. Table 2 lists the results of some recent measurements by Fricke and coworkers[48] of $G(Fe^{3+})$ for solutions of the above compositions. According to Thomas and Hart[44], $G(Fe^{3+})$ in an oxygen-saturated 10^{-2} M solution of Fe^{2+} in 0.4 M H_2SO_4 is 11.2 ions/100 eV at dose rates of $\sim 10^{11}$ rad s^{-1}.

Table 2. Values of $G(Fe^{3+})$ for the ferrous sulphate dosimetric system at high dose rates.

Dose rate, rad s^{-1}	$G(Fe^{3+})$, ions/100 eV	
	10^{-3} M soln. of Fe^{2+} in 0.4 M H_2SO_4 (saturated with air)	10^{-2} M soln. of Fe^{2+} in 0.4 M H_2SO_4 (saturated with O_2)
$\leqslant 10^8$	15.60	16.07
$7.14 \cdot 10^8$	15.33	16.07
$1.43 \cdot 10^9$	15.04	16.07
$2.86 \cdot 10^9$	14.55	16.02
$5.72 \cdot 10^9$	13.76	15.88
$1.14 \cdot 10^{10}$	12.68	15.65
$2.29 \cdot 10^{10}$	11.33	15.20
$5.58 \cdot 10^{10}$	9.64	14.61

Thus, an oxygen-saturated 10^{-2} M solution of Fe^{2+} in 0.4 M H_2SO_4 (often called the modified Fricke dosimeter) can be used to measure the dose of pulsed radiation at dose rates up to $\sim 6 \times 10^9$ rad s^{-1}.

The concentration of Fe^{3+} ions formed by irradiation is usually determined spectrophotometrically by measuring light absorption at 304 nm. The molar extinction coefficient of Fe^{3+} in 0.4 M H_2SO_4 is 2197 litre mole^{-1} cm^{-1} at 25°. Its temperature dependence[6] is 0.69% per degree.

5. OTHER AQUEOUS DOSIMETRIC SYSTEMS

The yield $G(Ce^{3+})$ in the cerium dosimetric system (10^{-4}–10^{-3} M solution of Ce^{4+} in 0.4 M H_2SO_4) has been found[41,42,44,46,51] to increase at dose rates above $\sim 10^8$ rad s^{-1}. For example, in a 2×10^{-4} M solution of Ce^{4+} in 0.4 M H_2SO_4 the yield $G(Ce^{3+})$ is ~ 3.3 ions/100 eV at a dose rate of $\sim 8 \times 10^9$ rad s^{-1},[51] as compared with 2.3–2.5 ions/100 eV for the same solution exposed to γ-radiation from ^{60}Co. Hence, the cerium system is not very useful for the dosimetry of pulsed radiation at dose rates in excess of $\sim 10^8$ rad s^{-1}.

According to Hutchinson[52], the yield of the bleaching reaction of Methylene Blue in aqueous solutions is drastically lowered under pulsed electron radiation conditions. Thus, the dose required to lower the optical density of a 5×10^{-6} M solution of this dye by 37% at a dose rate of $\sim 10^{10}$ rad s^{-1} is greater by a factor of 2–4 than at lower dose rates.

Bjergbakke and Sehested[53] studied the effect of dose rate under pulsed electron radiation conditions on $G(Fe^{3+})$ in a 5×10^{-3} M solution of H_2SO_4 containing 10^{-3} mole litre^{-1} of Fe^{2+} and 10^{-2} mole litre^{-1} of Cu^{2+}. They found that $G(Fe^{3+})$ in a deaerated solution is practically independent of dose rate up to 5×10^8 rad s^{-1}, whereas in an oxygen-saturated

solution the yield ceases to be constant at 10^8 rad s^{-1}. In the former solution $G(Fe^{3+})$ is 0.65, in the latter 0.75 ion/100 eV. The yield is independent of dose between 5×10^4 and 8×10^6 rad. At higher doses $G(Fe^{3+})$ begins to increase. At normal dose rates the value of $G(Fe^{3+})$ in this system is ~0.7 ion/100 eV.[53-56]

Feng and coworkers[54] published a more detailed study of the radiolysis of aqueous $FeSO_4$–$CuSO_4$–H_2SO_4 solutions at high dose rates. They found that $G(Fe^{3+})$ increases with dose rate, acidity, and oxygen concentration to ~4 ions/100 eV. However, the dependence of $G(Fe^{3+})$ on dose rate is much less marked when the solution contains large concentrations of Cu^{2+} ions. In a solution containing Fe^{2+}, H^+, O_2, and Cu^{2+} at the concentrations 10^{-3}, 10^{-2}, 2.4×10^{-4}, and 5×10^{-2} mole $litre^{-1}$ respectively, $G(Fe^{3+})$ is independent of dose rate up to ~$(1.0-1.4) \times 10^{10}$ rad s^{-1}. (The yield of Fe^{3+} under these conditions is 0.58 ion/100 eV) At slightly higher (0.1 M) concentrations of Cu^{2+} the yield remains constant up to a dose rate of ~3×10^{10} rad s^{-1}.

The yield of Fe^{2+} in a 5×10^{-3} M solution of H_2SO_4 saturated with air and containing Fe^{3+}, Cu^{2+}, and formic acid decreases at high dose rates[45]. Even at dose rates of ~10^8 rad s^{-1} the value of $G(Fe^{2+})$ in solutions containing large amounts of Cu^{2+} or HCOOH is lower than the yield for γ-radiolysis.

Sehested and coworkers[57,58] have studied the behaviour of an aqueous oxalic acid dosimeter at high dose rates. They found that the yield for the decomposition of oxalic acid (at a dose corresponding to 25% decomposition) is independent of dose rate up to 2×10^8 rad s^{-1} when the concentration of oxalic acid is up to 2×10^8, 2×10^9, and 2×10^{10} rad s^{-1} when the concentration of oxalic acid is 0.05, 0.1, and 0.2 M respectively. The yield for the decomposition of $H_2C_2O_4$ was 4.9 molecules/100 eV.

Anderson and Hart[59] measured the yield of radiolysis products in an oxygen-saturated solution containing 10^{-2} mole $litre^{-1}$ of HCOOH and 5×10^{-4} or 5×10^{-3} mole $litre^{-1}$ of H_2SO_4 at dose rates of ~3×10^9 rad s^{-1}. The results (in molecules/100 eV) are: $G(H_2O_2) = 3.25$, $G(CO_2) = 2.75$, $G(-O_2) = 2.82$, and $G(H_2) = 0.43$. These values are practically identical to the yields observed with γ-radiation from ^{60}Co.

Pikaev and Glazunov[45] found that $G(Fe^{3+})$ in deaerated sulphuric acid solutions of Fe^{2+} under pulsed electron irradiation is considerably lower than under γ-radiolysis conditions. Thus, $G(Fe^{3+})$ for a 3×10^{-3} M solution of Fe^{2+} in 0.4 M H_2SO_4 is ~6.7 ions/100 eV even at a dose rate of 5×10^7 rad s^{-1}.

The yield of phenol in solutions of benzene saturated with air or oxygen is strongly dependent on the dose rate of the pulsed radiolysis[9,60,61]. For example, $G(C_6H_5OH)$ is found[60,61] to be 0.8 molecule/100 eV at a dose rate of 3.6×10^9 rad s^{-1}, as compared with 1.9–2.1 molecules/100 eV during γ-radiolysis.

Pikaev and coworkers[61-63] found that in sulphuric acid solutions of Fe^{2+} containing oxygen and benzene or ethanol the $G(Fe^{3+})$ value decreases very substantially at high dose rates. For example, in a 2.5×10^{-4} M solution of Fe^{2+} in 0.4 M H_2SO_4 saturated with benzene and air the $G(Fe^{3+})$ value is ~15 ions/100 eV at a dose rate of ~5×10^8 rad s^{-1}, as compared with 64 ions/100 eV for γ-radiation from ^{60}Co in the same solution.[61,62]

Many workers[44,59,64-66] have studied the pulse radiolysis of water at different pH values. Fricke and Hart[6] recommend the use of a deaerated solution of H_2SO_4 at pH 3–4 for the dosimetry of pulsed radiation. In this solution, $G(H_2O_2) = G(H_2) = 1.16$ molecule/100 eV at dose rates up to ~2×10^9 rad s^{-1}.[65] According to Willis and coworkers[66], $G(H_2)$ in deaerated, neutral water decreases from ~1 to ~0.8 molecule/100 eV as the dose rate is increased from ~1.6×10^{12} to ~1.6×10^{14} rad s^{-1}. At a dose rate of ~1.6×10^{14} rad s^{-1}, $G(H_2)$ increases from 0.8 to 1.1 molecule/100 eV as the pH decreases from 7 to 1.

6. USE OF HYDRATED ELECTRON FORMATION IN DOSIMETRY

Hart and coworkers[6,67-71] suggested the use of the hydrated electron formation reaction in 10^{-2} M NaOH solutions saturated with hydrogen (7×10^{-4} mole $litre^{-1}$ H_2) in pulsed radiation dosimetry†. In these solutions the $e^-_{aq.}$ species produced by doses between 1 and 100–150 rad per pulse decay mainly by recombination.

The hydrated electron is characterised by a strong optical absorption in the visible region of the spectrum, with a band maximum at 720 nm. According to some recent measurements[73], the molar extinction coefficient of $e^-_{aq.}$ is 1.85×10^4 litre $mole^{-1}$ cm^{-1} at 715 nm. Evidently, the concentration of hydrated electrons can easily be measured spectrophotometrically. However, $e^-_{aq.}$ is a short-lived particle, with a half-life of ~25 ms in a solution of the above composition[69]. Hence, fast spectrophotometric methods must be used to measure the concentration of $e^-_{aq.}$: these methods are discussed in Refs. 1 and 2.

The dosimetric method consists in measuring the kinetics of the decay of optical absorption associated with the $e^-_{aq.}$ species. To calculate the dose from these measurements we need to know the initial optical density E_0 of the hydrated electron and the product $G.\epsilon$ (where ϵ is the extinction coefficient of $e^-_{aq.}$) at the chosen wavelength. The quantity E_0 is found by extrapolating the kinetic curve to $t = 0$ (where t is time). The value of $G.\epsilon$ at 700 nm for a hydrogen-saturated solution (pH 12) is 1.21×10^5 (litre $mole^{-1}$ cm^{-1})·molecules/100 eV. The formula for the dose D in this case is

$$D = \frac{0.994 \cdot 10^9 E_0}{1.21 \cdot 10^5 l} = 7.8 \cdot 10^3 \frac{E_0}{l} \text{ rad/pulse} \qquad (1)$$

where l is the optical path length of the measuring beam in the cell (in cm).

This dosimetric method enables[69] doses between 1 and 100–150 rad/pulse to be measured. With doses below 1 rad/pulse accurate measurements are difficult. With doses in excess of 100–150 rad per pulse the product $G.\epsilon$ begins to decrease because the transformation of OH into $e^-_{aq.}$ is incomplete. The upper limit of measurable dose can be raised by lowering the pH of the medium to 9 and by replacing H_2 by, for example, methanol (at a concentration to 10^{-3} M). In this solution H and OH are not converted into $e^-_{aq.}$, and therefore $G.\epsilon$ at 700 nm remains equal to 5.0×10^4 (litre $mole^{-1}$ s^{-1})·molecules/100 eV. Using this solution, doses per pulse up to 10^4 rad can be measured[6].

This dosimetric method cannot be used with pulses longer than a few microseconds[69], because the duration of the pulse must be kept shorter than the half-life of the $e^-_{aq.}$ species so that the recombination of $e^-_{aq.}$ during the pulse can be ignored. However, at low doses per pulse (~1 rad) the half-life of $e^-_{aq.}$ is long enough for pulses of 10^{-3} s duration to be acceptable. Fielden and Hart[69] showed that the limitations can be defined as

†The formation of $e^-_{aq.}$ by the radiolysis of aqueous systems and the properties of these particles are discussed in recent monographs[67,72].

follows: for doses of ~100 rad per pulse the minimum dose rate must be 10^7 rad s^{-1}, while for doses of ~1 rad the dose rate must be at least 10^3 rad s^{-1}. The dosimeter gives the same results for electron pulses and for pulses of X-rays.

The dosimetric solution can be used repeatedly. Fielden and Hart [69] obtained reproducible results over a period of 2 years, during which the total dose was greater than 1 Mrad, with a solution sealed in a quartz cell. Traces of oxygen present in the original solution are removed by a preliminary irradiation. If the solution is accidentally exposed to an excessive dose rate, the resulting hydrogen peroxide can be destroyed by irradiating the cell at a low dose rate.

Hart and Anbar [67] recommend, for measurements at high dose rates (up to 10^{10} rad s^{-1} with microsecond pulses and up to 10^{12} rad s^{-1} with nanosecond pulses), a method based on the steady-state concentration of hydrated electrons. In a solution free from acceptors for the e^-_{aq} particle the maximum concentration of these particles is reached at the end of the pulse. However, if the solution contains a relatively high concentration of electron acceptors, a steady-state concentration of e^-_{aq} is set up during the application of the pulse. The dose rate can be found by measuring this concentration, using the formula

$$I = \frac{k[S][e^-_{aq}]_{st} \cdot 6{,}02 \cdot 10^{25}}{G(e^-_{aq})} \qquad (2)$$

where I is the dose rate (eV litre^{-1} s^{-1}), k is the rate constant of the reaction between the acceptor S and e^-_{aq} (litre mole^{-1} s^{-1}), [S] and $[e^-_{aq}]$ are the molar concentration of S and the steady-state concentration of e^-_{aq} during the pulse, and $G(e^-_{aq})$ is the yield of e^-_{aq} (2.7 electron/100 eV).

Perchloric acid at 10^{-3}–10^{-2} M concentration can be used as the acceptor for e^-_{aq}. The value of k for H^+ ions is 2.2×10^{10} litre mole^{-1} s^{-1}. [74] The main weakness of this method is that $G(e^-_{aq})$ may be a function of the acceptor concentration [75].

Evidently, the most serious drawback of these methods of dosimetry is the complicated equipment needed to measure the optical absorption of e^-_{aq}. Hence, these methods are used only in laboratories already committed to pulse radiolysis studies with optical monitoring of short-lived particles.

7. DOSIMETERS BASED ON POLYMER SYSTEMS

Various polymers have bean suggested for the dosimetry of pulsed radiation. Boag [76] recommends the use of plates of poly(methyl methacrylate) between 1 and several millimeters thick. Irradiation of this polymer produces optical absorption with a maximum at 292 nm. The optical density at this wavelength is linearly related to the dose in the range from 5×10^4 to ~10^6 rad.

Harrah [77,78] used polystyrene and polyhalogenostyrene plates containing various additives. He showed [77] that polystyrene plates containing *trans*-stilbene are suitable for dose measurements in the range 2×10^5–10^8 rad at dose rates between 300 and 7.5×10^{13} rad s^{-1}. Under these conditions the effect is independent of the energy of the radiation over the range 1.25×10^{-3}–4.7 MeV. The plates were prepared from benzene solutions of polystyrene (10 wt.%) and *trans*-stilbene (0.025 wt.%). Irradiation induces the isomerisation of *trans*-stilbene into the *cis*-isomer. This transformation is conveniently monitored spectrophotometrically from the absorption of light at 324 nm: at this wave length the extinction coefficient of *trans*-stilbene is more than an order of magnitude greater than the extinction coefficient of *cis*-stilbene. The measurement consists in finding the ratio $R = (D_0 - Dt)/D_0$, where D_0 is the initial optical density of the plate at 324 nm and Dt is the optical density after absorption of the dose. The radiation-chemical yield of the disappearance of *trans*-stilbene is 0.73 molecule/100 eV. The precision of this method is ±5% at doses greater than 1.5×10^6 rad, and ±10% at lower doses.

In his next paper [78], Harrah showed that polyhalogenostyrene plates containing the methoxide of Malachite Green can be used to measure doses between 5×10^4 and 1.5×10^7 rad at dose rates up to 10^{14} rad s^{-1}. The plates were prepared from benzene or chloroform solutions containing 10 wt.% of the polymer and 0.1 wt.% of the dye. The dye was used in its leuco-form, obtained by slowly adding a methanol solution of Malachite Green to a 1 M solution of sodium methoxide with vigorous stirring, followed by recrystallisation from benzene after treatment with activated charcoal. Irradiation induces a colour in the plate. The intensity of the colour is measured spectrophotometrically from the light absorption at 630 nm (for doses up to ~3×10^6 rad) or at 430 nm (for doses of 10^6–1.5×10^7 rad). The extinction coefficient of the dye at 430 nm is ~20% of the extinction coefficient at 630 nm. The effect of dose rate was tested with poly(4-chlorostyrene) plates. The measured optical densities at dose rates up to ~10^{14} rad s^{-1}, produced by electron pulses 2×10^{-8} s long (electron energy 2 MeV), differed by no more than 2% from those obtained with dose rates of 300 rad s^{-1} of γ-radiation from ^{60}Co. For a dose rate of 10^{15} rad s^{-1} the difference increases to 8%. All measurements were done in vacuum. In the presence of air the sensitivity of the films to γ-radiation is 25% higher than for vacuum irradiation. With poly(4-bromostyrene) plates the effect of oxygen is less marked (only ~4%). The existence of an oxygen effect is one of the drawbacks of this method of dosimetry. Another drawback is the marked dependence of the results on the presence of impurities in the plates.

Willis and coworkers [26] examined the possibility of using blue Cellophane films marketed by the firm of Dupont (USA) for the dosimetry of pulsed radiation from an accelerator of the "Febetron" type. These films contain the dye dimethoxyphenyl-*bis*-azo-*bis*-8-amino-1-naphthol-5,7-disulphonic acid [79], which is bleached by irradiation. The extent of bleaching is measured in a spectrophotometer at 655 nm. Willis and coworkers found that these films can be used to measure doses between 5×10^5 and 1.4×10^7 rad.

The energy of the radiation is not fully absorbed in the films, which must therefore be calibrated and can be used only as relative dosimeters.

8. ORGANIC LIQUIDS AS DOSIMETRIC SYSTEMS

Willis and coworkers [26] found that $G(H_2)$ for the radiolysis of liquid benzene by pulsed electrons generated by a "Febetron 705" accelerator (dose rate 10^{14} rad s^{-1}) is 0.04 molecule/100 eV. Thus, the yield of hydrogen is almost the same as reported [80–82] for lower dose rates (0.036–0.040).

The same workers pointed out a special feature of dosimetric measurements at very high dose rates using benzene (and possibly also other liquids of low electrical conductivity). Each pulse injects a charge of a few hundredths of a microcoulomb into the liquid. The relaxation time of the conductivity in these liquids is of

the same order as (or greater than) the duration of the pulse ($\sim 3 \times 10^{-8}$ s). Hence, the strong electric charge induced in the liquid by the leading edge of the pulse will tend to repel the electrons arriving during the main period of the pulse, and the measured dose will be seriously in error. Obviously, the magnitude of this effect increases with the thickness of the sample. It is found[26] to be negligible with sample thicknesses of 0.2–1.0 cm (for which $G(H_2) = 0.04$ molecule/100 eV), but it becomes significant with benzene samples 1.5 cm thick, for which $G(H_2) = 0.02$–0.03 molecule/100 eV.

Boyd and coworkers[83] studied the radiolysis of cyclohexane by electron pulses at dose rates up to $\sim 10^{14}$ rad s^{-1}. Under these conditions $G(H_2)$, though smaller than in γ-radiolysis, remains constant (14 molecules/100 eV) for dose rates between 6×10^{12} and 1.3×10^{14} rad s^{-1}. $G(H_2)$ is also independent of dose over the range which was explored (4×10^5–2.4×10^7 rad).

Dvornik and coworkers[84] recommend the use of ethanolic solutions of chlorobenzene containing 4 vol.% of water for the dosimetry of pulsed electronic radiation. With this system, the dose is measured by the formation of H^+ or Cl^- ions. They found that if the solution contains more than 10 vol.% of C_6H_5Cl the value of $G(HCl)$ is practically the same for γ-rays from ^{60}Co and for pulsed electron radiation at a dose rate of 10^9 rad s^{-1} (pulse length 7×10^{-6} s, electron energy 10 MeV). The following values of $G(HCl)$ were obtained for different concentrations of C_6H_5Cl (shown in brackets as vol.%): 4.53(10), 4.95(15), 5.19(20), 5.34(30), and 5.47(40).

9. GASEOUS DOSIMETRIC SYSTEMS

The possibility of using ethylene, oxygen, and nitrous oxide as dosimetric systems for pulsed electronic radiation has been investigated[15,85–89]. $G(H_2)$ for the radiolysis of ethylene at dose rates of $\sim 10^{14}$ rad s^{-1} is found[15] to vary with pressure. The yield of hydrogen decreases from 1.9 to 1.04 molecule/100 eV as the pressure is increased from 0.5 to 10 atm. In the γ-radiolysis of ethylene (at 1 atm pressure) $G(H_2) = 1.31$ molecule/100 eV.[90]

The yield of ozone in the radiolysis of gaseous oxygen by electron pulses (dose rate 10^{12}–3×10^{13} rad s^{-1}) is much higher than in γ-radiolysis[87–89,91]. According to Willis and coworkers[88], $G(O_3) = 12.8 \pm 0.6$ molecules/100 eV at the above dose rates, whereas only 6.2 ± 0.6 molecules of O_3 are produced by 100 eV in γ-radiolysis. The dose rate at which $G(O_3)$ begins to vary has not been identified precisely. Hence, oxygen can be used as a dosimetric system only at dose rates in the range 10^{12} to 3×10^{13} rad s^{-1}, for which $G(O_3)$ is known[88] to have a constant value of 12.8 molecules/100 eV. Under these conditions $G(O_3)$ remains constant over the pressure range 0.04–1 atm and for total doses in the range 0.05 to 0.35 Mrad. The ozone produced by the electron pulses is conveniently detected spectrophotometrically by light absorption at 254 nm. Its extinction coefficient at this wavelength[92] is 132 cm^{-1}, or[93] 135 cm^{-1} (both values being reported for normal pressure and temperature). Alternatively, the ozone can be determined iodometrically when higher precision is required. Boyd and coworkers[94] have recently made a detailed study of the reaction between I^- and O_3: they find that at pH 7 one molecule of O_3 generates 1.53 molecules of I_2.

In the radiolysis of gaseous nitrous oxide, $G(N_2)$ increases by approximately 20% as the dose rate is raised from the $\sim 10^2$–10^3 rad s^{-1} level to $\sim 10^{12}$ rad s^{-1}. The yield for γ-radiolysis[95] is ~ 10 molecules/100 eV, rising to 12.4 molecules/100 eV for radiolysis by powerful electron pulses[15,85,86]. For N_2O at 1 atm pressure, the change in yield occurs[86] in the range of dose rates 1.6×10^8–1.6×10^{11} rad s^{-1}. In pulse radiolysis, $G(N_2)$ is independent of N_2O pressure between 0.5 and 5.0 atm.[15] At 1 atm pressure the yield does not vary[85] if the temperature is raised to 200°. The yield is insensitive to dose up to 6.4×10^6 rad. According to Willis and coworkers[96], $G(N_2)$ equals 12.4 molecules/100 eV even at dose rates as high as $\sim 3 \times 10^{14}$ rad s^{-1}.

Boyd and coworkers[97] discovered an interesting feature of the dosimetry of pulsed electron radiation by means of gaseous systems. They studied the effect of pressure on the radiolysis yields of gaseous HCl, HBr, and N_2O at a dose rate of 1.6×10^{13} rad s^{-1}, and they found that below 0.5 atm the yield of H_2 in HCl and HBr is much higher than above 1 atm. (The same is true of the yield of N_2 in N_2O.) The effect is ascribed to the acceleration of secondary electrons in the transient electric field generated by the powerful electron pulses. A similar phenomenon occurs[96] in the radiolysis of N_2O and H_2S by electrons at a dose rate of $\sim 3 \times 10^{14}$ rad s^{-1}.[96]

Gaseous dosimetry at dose rates above 10^{12} rad s^{-1} is carried out in cells made of stainless steel. Lampe and coworkers[98] noticed a catalytic effect of this material in the decomposition of nitrous oxide of γ-radiolysis. The increase in the nitrogen yield due to this effect, $\Delta G(N_2)$, is described by the empirical formula

$$\Delta G(N_2) = \frac{4.2}{PI}, \qquad (3)$$

where P is the pressure of N_2O (atm) and I is the dose rate (Mrad h^{-1}).

It follows from formula (3) that for $P = 1$ atm and $I >$ 10 Mrad h^{-1} the quantity $\Delta G(N_2)$ is small in comparison with $G(N_2)$, which is usually 10–13 molecules/100 eV. Evidently, the effect can be ignored in pulse radiolysis, for which $I \gg 10$ Mrad h^{-1}.

10. OTHER DOSIMETRIC SYSTEMS

The output of the LiF thermoluminescent dosimeter is reported[99–101] to be independent of dose rate up to 2×10^{11} rad s^{-1}. It is also independent of dose[101] up to 10^5 rad.

Fielden and Hart[69] made a detailed study of the suitability of LiF single crystals for the dosimetry of pulsed radiation. They found that the response of this dosimeter is independent of dose rate between 0.9 and 1.5×10^6 rad s^{-1}. The measurements were made with γ-radiation from ^{60}Co and with X-ray pulses of different duration (10^{-6}, 9.5×10^{-8}, and 1.1×10^{-8} s). These authors stress that LiF can be used to measure extremely small doses (down to 10^{-2} rad per pulse).

Lithium fluoride has also been examined by Alsop and coworkers[102] as a possible thermoluminescent dosimeter for electron pulses at dose rates up to 10^{12} rad s^{-1}. These workers also considered the possibility of using CaF_2, activated with Mn, for the dosimetry of this type of radiation.

Schmidt and Buck[103] proposed a calorimetric method for the dosimetry of pulsed electronic radiation in which thermal changes are monitored conductimetrically. Their quartz cell, fitted with two parallel platinum foil electrodes, is filled with electrolyte and placed behind the collimator which defines an electron beam 2.5 cm in diameter. When the electron pulse strikes the cell, the

Table 3. Dosimetric systems for pulsed radiation.

System	Indicator reaction	Radiation-chemical yield (ions or molecules/100 eV)	Dose rate (rad s^{-1}) for constant radiation-chemical yield
10^{-3} M aq. Fe^{2+}, 0.4 M H_2SO_4, saturated with air	Formation of Fe^{3+}	15.6	$<10^8$
10^{-2} M aq. Fe^{2+}, 0.4 M H_2SO_4, saturated with oxygen	ditto	16.07	$<6 \times 10^9$
10^{-4}–10^{-3} M aq. Ce^{4+}, 0.4 M H_2SO_4	Reduction of Ce^{4+}	2.3–2.5	$<10^8$
10^{-3} M aq. Fe^{2+}, 10^{-2} M Cu^{2+}, 5×10^{-3} M H_2SO_4, deaerated	Formation of Fe^{3+}	0.65	$< 5 \times 10^8$
10^{-3} M aq. Fe^{2+}, 10^{-2} M Cu^{2+}, 5×10^{-3} M H_2SO_4, saturated with oxygen	ditto	0.75	$<10^8$
10^{-3} M aq. Fe^{2+}, 5×10^{-2} M Cu^{2+}, 10^{-3} M H_2SO_4, saturated with air	"	0.58	$<10^{10}$
10^{-3} M aq. Fe^{2+}, 0.1 M Cu^{2+}, 10^{-2} M H_2SO_4, saturated with air	"	0.58	$<3 \times 10^{10}$
5×10^{-2} M aq. $H_2C_2O_4$	Decompn. of $H_2C_2O_4$	4.9	$<2 \times 10^8$
0.1 M aq. $H_2C_2O_4$	ditto	4.9	$<2 \times 10^9$
0.2 M aq. $H_2C_2O_4$	"	4.9	$<2 \times 10^{10}$
10^{-2} M solution of NaOH, saturated with hydrogen	Formation of e^-_{aq}	6.6	$<1.5 \times 10^8$
10^{-3} M solution of CH_3OH (pH 9)	ditto	2.7	$<10^{10}$
aq. H_2SO_4 (pH 3–4)	Formation of H_2O_2 or H_2	$G(H_2O_2) = G(H_2) = 1.16$	$<2 \times 10^9$
Benzene	Formation of H_2	0.04	6×10^{12}–$1.3 < 10^{14}$
Cyclohexane	ditto	4	
Chlorobenzene in ethanol, containing 4 vol.% H_2O	Formation of HCl	4.5–5.5 (depending on concn. of C_6H_5Cl)	up to 10^9
Gaseous oxygen	Formation of ozone	12.8	10^{12}–3×10^{13}
Gaseous nitrous oxide	Formation of N_2	12.4	1.6×10^{11} and above
Polystyrene plates containing *trans*-stilbene	Stilbene isomerisation	0.73	up to 7.5×10^{13}
Polychlorostyrene plates containing the methoxide of Malachite Green	Colouration of plate	—	up to $\sim 10^{14}$
LiF single crystals	Thermoluminescence	—	up to 2×10^{11}–10^{12}

emperature of the electrolyte rises due to the absorption of the dose, and the electrical conductivity also changes by ~ 2% per degree). Changes in electrical conductivity are measured by a sensitive bridge method. This calorimetric cell can be used for doses of $\sim 10^3$ rad. The best electrolyte is a phosphate buffer (pH ~ 7), in which changes of electrical conductivity due to radiation-chemical reactions are negligible. A correction for the energy absorbed by the platinum foil electrodes must be made.

5.1. DOSE MEASUREMENT ALONG THE LIGHT BEAM DURING PULSE RADIOLYSIS WITH OPTICAL MONITORING OF SHORT-LIVED PARTICLES

As was pointed out earlier in this review, when optical monitoring of the short-lived particles is used in pulse radiolysis it is necessary to know the dose along the path of the light beam used as a probe. This is because the distribution of the dose is not usually uniform in these experiments (for example, only part of the solution is exposed to the radiation, the cross-section of the light beam is smaller than the cross-section of the electron beam, etc.). In these systems the dose is measured from observations of the optical absorption of any reaction product whose optical characteristics are known.

Dorfman and coworkers [104,105] suggest, for dosimetry under these conditions, measurement of the optical absorption of the Fe^{3+} ions produced during the irradiation of a solution of ferrous sulphate in sulphuric acid. In this system the kinetic curve shows a stationary period lasting several seconds after the application of the pulse. Adams and coworkers [106] used an aqueous solution of ferrocyanide, in which the plateau of the kinetic curve is reached in a few milliseconds. Fletcher and coworkers [107] used a $\times 10^{-3}$ M solution of KCNS saturated with oxygen, in which $(CNS)_2^-$ ion-radicals are formed by the reaction between OH radicals and thiocyanate ions. The molar extinction coefficient of this particle is 7350 litre $mole^{-1}$ m^{-1} at 475 nm, and $G[(CNS)_2^-] = G(OH) = 2.9$. [108,109]

Other workers [110–112] also used a CNS^- solution for this purpose. The formation of hydrated electrons (see Section 6) is a possible alternative approach to this problem.

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This review has highlighted a number of special features of chemical methods of dosimetry when applied to pulsed radiation as opposed to γ-radiolysis. The most important effect is a dependence of the yield of the radiolysis products upon the dose rate: hence, it is essential to choose a dosimetric system whose response is independent of dose rate within the expected range. Table 3 has been compiled to assist the reader in the choice of a suitable system.

The following conclusions can be made by inspection of Table 3. Liquid benzene is the most generally applicable dosimetric system. The yield of hydrogen during radiolysis of liquid benzene is constant over the entire range of dose rates likely to be available to present-day workers. With aqueous solutions, the range of dose rates over which the yield is constant usually increases with solute concentration. The most convenient gaseous system for the dosimetry of pulsed radiation is nitrous oxide, because the yield of N_2 varies only by 20% between γ-radiation and electronic radiation from an accelerator of the "Febetron" type. Lastly, chemical changes in some polymer systems can also be independent of dose rate between wide limits.

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