Chapter 2

Tools for radiolysis studies

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Since the first report of the chemical effects of radiation by Pierre and Marie Curie, researchers have needed tools to deliver ionizing radiation for their scientific studies in increasingly precise ways. In the earliest stages, this was accomplished by the development of radioactive sources of increasing refinement and activity, and by the construction of X-ray tubes of increasing power. In the middle of the 20th Century, particle (primarily electron) accelerators took over as the primary tools of radiation chemists. At first, these accelerators were employed as continuous radiation sources like their predecessors. However, the development of pulse radiolysis techniques in the 1960s vastly increased the ability to study radiation-induced chemical kinetics. Before long, time resolution was extended into the picosecond regime [1-5]. In recent years, a new generation of radiolysis facilities has been developed to extend temporal resolution to even shorter times, at the same time providing a range of new transient detection capabilities [6-13].

Detailed accounts of the development of radiation chemistry and its tools can be found elsewhere. The purpose of this chapter is to describe the basic characteristics of continuous and pulsed sources of ionizing radiation for radiolysis studies, and to provide a broad overview of the present and near-future status of radiolysis instrumentation worldwide, for the benefit of readers who would like to use these powerful techniques to advance their own research. It is inevitable under the circumstances that some facilities may be missed and that future developments will soon render this overview out-of-date, however the substantial progress that has been made in the years since the previous reviews appeared [14-16] merits description here.

Types of ionizing radiation and their methods of generation

Ionizing radiation for chemical studies comes in many types with a vast range of properties that allow adaptation of experimental design to the chemistry of interest. The fundamental point to remember is that radiolytic energy deposition within the sample is inhomogeneous on short time (nanosecond) and length (nanometer) scales, and that the spatial pattern of reactive species produced from this energy deposition depends on the type of incident radiation and its energy. Photonic radiations (X- and gamma rays) deposit energy in well-separated interactions within the sample, while highly charged nucleons produce much denser deposition patterns with a higher probability of overlapping regions of ionized species. This effect is quantified as "Linear Energy Transfer" or LET. Photons and electrons are considered to be low LET radiations, whereas protons and heavier nucleons are high LET. There is also a dependence of LET on particle kinetic energy. Reactions of (and between) primary radiation-produced species convert the spatial inhomogeneity into variations in yield of radiolysis products on longer time scales (microseconds and beyond) depending on the type and energy of radiation. Chapter 1 of this book and other publications [14-17] discuss these effects in greater detail. The experimental choice of radiation type and energy depends on the application. Electron beams and X-rays (gammas) are well suited for general kinetics studies, while high LET radiations provide important details about the physical mechanisms of radiolysis and its chemical effects, and they are also becoming quite important in the study of clustered damage in nanostructured materials, including biological systems (DNA and cells) and synthetic polymers and resists (*e.g.*, ion beam lithography).

X- and gamma rays

Ionizing photonic radiation (X- and gamma rays) can be produced by the decay of certain radioactive isotopes or generated by stopping or deflecting a particle beam (*bremsstrahlung* and synchrotron radiation, respectively). X- and gamma rays, by virtue of their low LET, can penetrate sample vessels of moderate thickness such as cryostats or pressure vessels, however by the same token the deposited radiolytic dose (energy per unit sample mass) is low compared to particle radiations of the same fluence. Radioactive gamma sources based on ^{60}Co or ^{137}Cs isotopes are used in continuous radiation mode for radiolysis product studies and competition kinetics measurements. There are two basic types of source-based irradiators for chemical research. In the first, samples are placed within a shielded vault containing a radioactive source in a shielded container. After the experimenter exits the vault, the source is removed from the shielded container to expose the samples. In a modification of this design, samples may be transported into and out of the irradiation vault by a conveyor system. The second type of irradiator consists of a hollow cylindrical

radioactive source permanently fixed in shielding. A mechanism is used to transport samples into the center of the cylindrical source, where they receive uniform radiation by virtue of the geometry. Due to the configuration, sample dimensions are limited to what will fit inside the source cylinder. Some gamma irradiators can be fitted with flow systems that transport fluids through the irradiation zone for controlled exposure times.

Particle accelerators can be used as continuous or pulsed X-ray sources by stopping the particle beam (typically electrons) in a high-atomic-number material such as gold or tungsten. The process of *bremsstrahlung* ("braking radiation" in German) produces a broad continuum of X-radiation that peaks at one third of the incident particle energy. This method can be used to produce nanosecond or picosecond X-ray pulses for time-resolved kinetics studies. For example, accelerator-produced X-rays were used to initiate experiments to measure the mobilities of excess electrons in non-polar liquids as functions of temperature and pressure, using transient conductivity measurement techniques. The experiments depend on the ability of X-rays to penetrate pressure vessel walls that would stop particle beams.

Other types of accelerators can be used as X-ray sources for specialized purposes. Synchrotron facilities can provide very intense radiation over a wide but selectable range of energies. Depending on the operating mode of the synchrotron it is possible to do time-resolved studies. Extremely short, sub-picosecond pulses of X-rays can be generated by laser wake-field accelerators (described below), which use terawatt electromagnetic fields from femtosecond lasers to accelerate electrons but also produce intense pulses of X-rays. When a second femtosecond laser pulse is used to interrogate the sample at various delay intervals with respect to the X-ray pulse, it would be possible to follow the very earliest steps of the radiolytic process.

Because of their high intensity, X-ray tubes were commonly used as laboratory radiation sources for radiation chemistry experiments until they were superceded by particle accelerators during the middle part of the 20th Century. They still retain specialized uses in research applications such as being used as the radiation source for MARY (MAgnetic field effect on Reaction Yield) spectroscopy studies of radical cation lifetimes and reactivity in alkane solvents [14,18]. MARY spectroscopy uses fluorescence to detect variations in singlet-triplet dynamics in radical ion pairs as a function of magnetic field. It is particularly useful for short-lived transients that are difficult to study by ESR.

Particle accelerators for radiolysis

There are several methods used to accelerate charged particle beams for pulse radiolysis. Acceleration requires a force applied by an electric field. The field may be a continuous

gradient (or "DC" as in direct current) as produced by an electrostatic potential (**Fig. 1a**), or oscillating in time and space as produced by radio frequency (RF), microwave, or optical laser radiation (**Fig. 1b**).

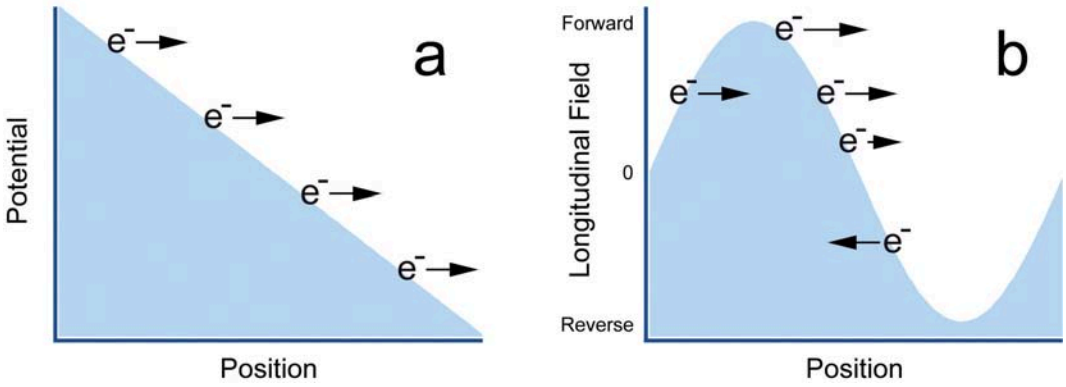

Figure 1: *Schematic depictions of electrostatic (a) and oscillating electromagnetic (b) fields for charged particle acceleration.*

Examples of the electrostatic type of accelerator are the Van de Graaff generator and capacitor-driven DC impulse generators. The characteristics of the two are quite different. The Van de Graaff generator (**Fig. 2**) develops and maintains a continuous electrostatic field by transporting charge (typically electrons) on a belt of non-conducting material that passes between two terminals at ground and high potential, respectively. The terminals are separated by stacks of insulating material alternating with metal plates. The metal plates are each connected to a resistor chain that slowly drains the charge off the high potential terminal so that the accelerating potential can be controlled by the belt charging rate. Typical operating potentials of such accelerators are 2-5 MV. Standing electrostatic potentials higher than 5 MV become progressively more difficult to sustain without extraordinary measures, and beam energies of 2-5 MeV are adequate for many pulse radiolysis applications. An evacuated beam tube runs from the high-potential terminal to ground. The insulating glass spacers along the tube are interrupted at intervals by the metal plates connected to the resistor chain, so that a uniform accelerating gradient is applied to the particle beam.

Electron beams are by far the most common usage of Van de Graaff generators for pulse radiolysis, although ion sources may also be used. Typically, grid-gated cathodes are used to produce electron pulses varying in length from several nanoseconds to several microseconds with beam currents on the order of one Ampere. On some systems, continuous emission is possible at significantly lower currents (~ 1 mA). The minimum pulse width is determined by the response of the pulsing circuit. Specialized circuitry providing a

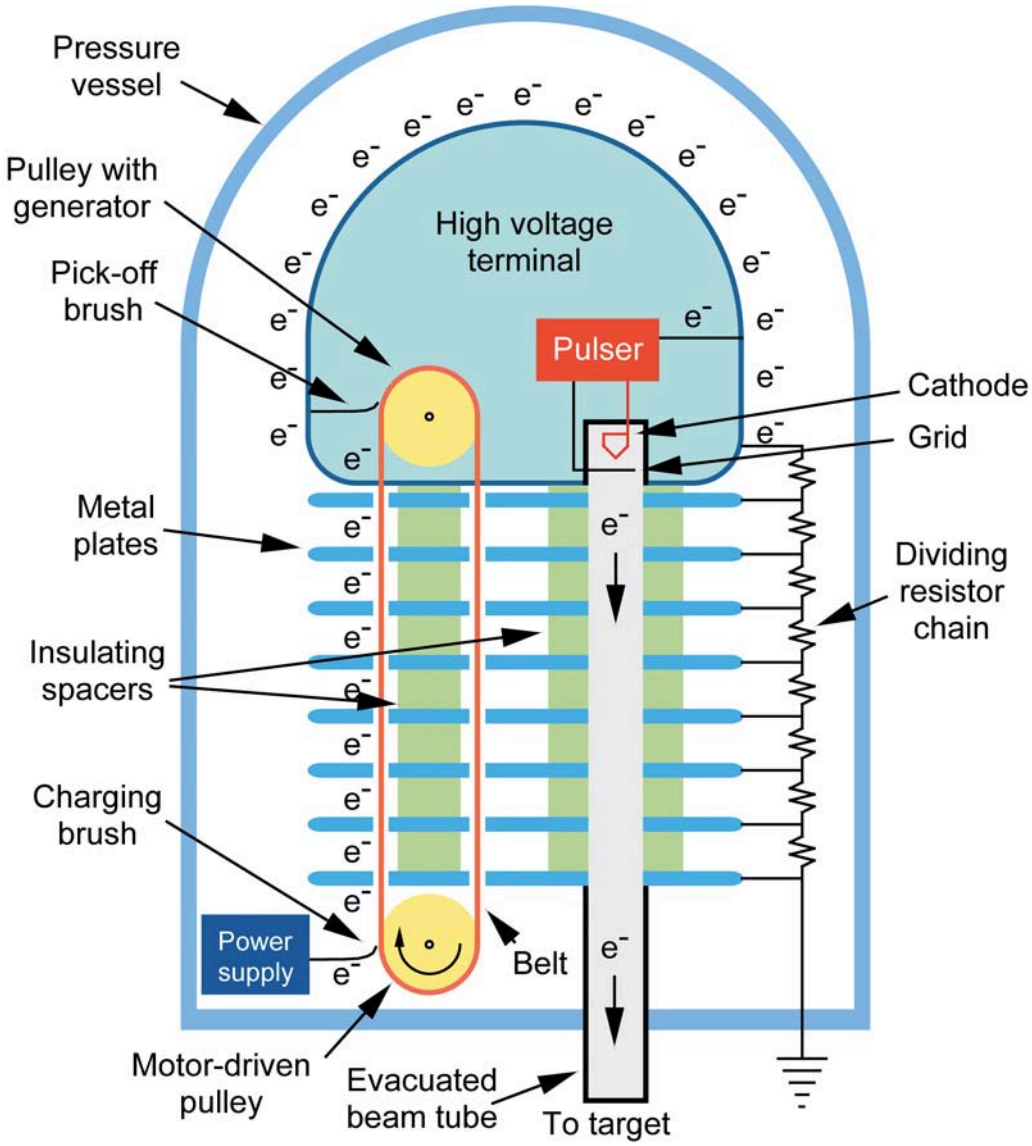

Figure 2 : *A Van de Graaff accelerator.*

sub-nanosecond electron pulse was developed on the 3 MV Van de Graaff accelerator at the Technical University of Delft [19]. Van de Graaff accelerators emit no electromagnetic noise apart from the impulse generated from the electron beam itself, since they are electrostatic devices. This is an advantage for the implementation of real-time detection systems such as time-resolved microwave conductivity (TRMC) and transient electron paramagnetic resonance (EPR). The Delft Van de Graaff has been the site of significant development of

the TMRC technique, which measures the migration and recombination processes of charge carriers in materials [20]. Transient EPR detection is useful for identifying and observing the reactions of radical species that are difficult to characterize by optical absorption spectroscopy [21]. A 3 MeV Van de Graaff accelerator with EPR detection system is located at the Notre Dame Radiation Laboratory (NDRL) in the United States. NDRL also hosts a time-resolved resonance Raman spectroscopy (TRRR) system on a 2 MeV Van de Graaff. The high specificity of vibrational spectroscopy provides information about the structure of radical species [22]. The 4 MeV ELBENA Van de Graaff at the Hahn-Meitner Institute in Berlin supports advanced transient absorption detection capabilities as well as AC and DC conductivity detection methods with nanosecond time resolution (DC) [23] The 2 MeV Van de Graaff at Brookhaven National Laboratory incorporates a sensitive transient absorption detection system and time-of-flight charge carrier mobility measurements in non-polar media by DC conductivity.

The second series of electrostatic accelerators are based on direct-current impulse generators. The best-known examples of these are the Febetron units produced by the Field Emission Corporation. These machines are based on a Marx-bank impulse generator, whereby a high (0.6 to 2.3 MV) potential is generated by triggering a series of spark gaps to switch a bank of capacitors from charging in parallel to discharging in series through a large cathode tube. Very large electron currents (~ 7000 A) are passed in pulses lasting several to tens of nanoseconds, delivering radiolytic doses up to 20 kGy. The large doses are well suited for the study of radical-radical reactions and the radiation chemistry of gases. The electrical noise generated by the spark gaps and the discharge of the Febetron is a major problem for detection systems, requiring much signal averaging and background correction, however the Febetron is unmatched in its ability to deliver large radiolytic doses in short pulse durations. Although Febetron-based pulse radiolysis facilities were once located in many laboratories, today only a few remain, notably a 600 keV unit at the Laboratoire de Chimie Physique of the University of Paris XI, in Orsay, France.

Another kind of impulse generator-based accelerator based on a pulse transformer was developed in Novosibirsk, USSR, in the 1970s. One such unit (ELIT-1, 1 MeV) has been operating at the Time-Resolved Spectroscopy Laboratory of the University of Leipzig. It is equipped with a beam deflection unit that can reduce the electron pulse width within the sample to less than a nanosecond and it has been coupled to a Fourier transform EPR detection system.

Accelerators that use electromagnetic radiation to produce the accelerating field can accelerate particles to much higher energies than electrostatic accelerators. Higher beam energies provide more penetrating power for elaborate experimental setups such as

pressure vessels and cryostats, and the ability to better focus more charge into a smaller target to produce a higher radiolytic dose. As a practical consideration however, beam energies above 40 MeV (for electrons) are less desirable for pulse radiolysis because an increasing fraction of the beam energy is converted into *bremsstrahlung* instead of being deposited in the sample in radiolytic events. In addition, the *bremsstrahlung* produced by high-energy beams can induce radioactivity in typical substances found in scientific equipment and building materials, creating an additional safety hazard.

Linear accelerators (or linacs) are the most common type of oscillating-field accelerator for pulse radiolysis. The accelerating sections consist of a series of resonant cavities for radio-frequency or microwave radiation (100 MHz to 10 GHz, with 1-3 GHz being most common). Charged particles are accelerated by the oscillating electric field to different degrees depending on their position (phase) with respect to the RF cycle. The differential acceleration collects the particles into bunches that are clustered around the optimal acceleration phase in each RF cycle. This fact underscores a significant difference in beam temporal profile between electrostatic and oscillating field accelerators. Beams emitted from the former type are continuous for the duration of the emission, whereas for the latter the beam is structured into a pulse train or "macropulse" consisting of a series of bunches separated in time by the period of the accelerating radiation. Each bunch is inherently short in time (~ 30 picoseconds); but significant technical effort is required to exploit the time resolution offered by such a short pulse, as explained below.

The majority of linear accelerators used for pulse radiolysis work exclusively in the pulse train mode and are typically referred to as "nanosecond" linacs, in contrast to the "picosecond" linacs that can operate in the single bunch mode. Nanosecond linacs for pulse radiolysis are distributed throughout the world, including the Notre Dame Radiation Laboratory in the U.S., the Commissariat à l'Énergie Atomique (CEA) in Saclay, France, the Institute of Applied Radiation Chemistry in Łódź, Poland, the Institute for Nuclear Chemistry and Technology in Warsaw, Poland, the ISOF-CNR in Bologna, Italy, the Institute of Isotope and Surface Chemistry in Budapest, Hungary, the Bhabha Atomic Research Center (BARC) in Mumbai, India, the National Centre for Free Radical Research in Pune, India, the Australian Radiation Protection and Nuclear Safety Agency in Melbourne, the University of Auckland, New Zealand, and at the Shanghai Institute of Nuclear Research in China. A linac for pulse radiolysis will be installed at the University of Manchester, UK, as part of the establishment of a new research group in Radiation Chemistry. Transient optical absorption spectroscopy is the standard technique for kinetics measurements at each of these facilities. In addition, transient mid-infrared detection methods are under development at the linac in Saclay [24].

Picosecond electron linacs require special techniques to generate single electron bunches for ultrafast kinetic studies. The problem stems from the fact that it is not practical to electrically gate a cathode electron source on and off in less than a nanosecond, thus cathode gating is too slow to fill only one period (350 to 770 ps) of the RF cycle at the accelerating frequencies of typical accelerators. In a clever development, a sweeping beam deflection device was used on the nanosecond Novosibirsk linac to select a single picosecond bunch from the pulse train [5]. Kinetics of charge recombination were followed by using a streak camera to monitor emission from excited states produced *via* electron-hole recombination. Aside from that special case, historically the standard method of generating picosecond single pulses (**Fig. 3**) is to inject the electrons into a lower frequency RF field operating at a sub-harmonic of the accelerating frequency (for example, 476 MHz for an S-band, 2856 MHz linac), allow the electron packet to evolve into a compact single bunch in the lower-frequency section, then to inject the compressed bunch into the higher-frequency accelerating section. The system used for injecting the single bunches is called a "sub-harmonic pre-buncher".

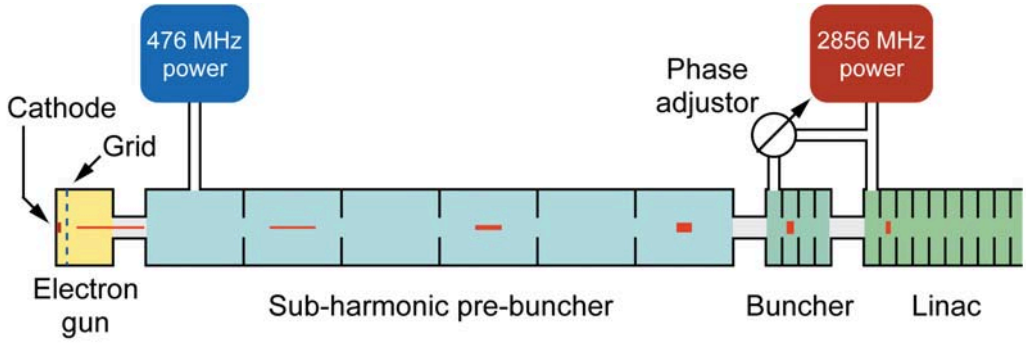

Figure 3 : *Schematic representation of an S-band pre-bunched picosecond linear accelerator.*

Because it involves more accelerating structures with multiple RF frequencies and phase relationships, and a high-performance electron gun source to inject the electrons in about one nanosecond, a sub-harmonic pre-buncher adds a lot of cost and complexity of operation of the linac facility. Consequently, only a few pre-bunched picosecond linacs were built for pulse radiolysis studies. The first one was installed at Argonne National Laboratory in the 1970s [2] ; subsequently other picosecond installations were built at the University of Tokyo Nuclear Energy Research Laboratory (NERL) in Tokai-Mura [3,4] and Osaka University [4]. Very recently, a new pre-bunched linac for pulse radiolysis has been built at the Shanghai Institute of Applied Physics.

During the late 1980s and into the 1990s, a new technology arose for generating picosecond electron beams [14,15]. Instead of using thermionic emission from a hot cathode

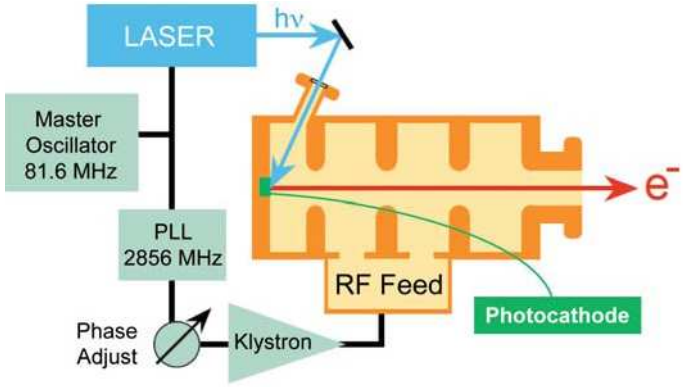

Figure 4 : *Schematic representation of the BNL LEAF photocathode electron gun accelerator showing the laser-microwave synchronization relationship.*

to produce the electron beam, a metal (Cu or Mg) or semiconductor (*e.g.*, Cs_2Te) cathode is struck with an ultraviolet laser pulse to cause it to emit electrons via the photoelectric effect. The electron pulse emitted from the photocathode is as short as the incident laser pulse (although it tends to expand during beam transport). Thus it is possible to inject single bunches of electrons directly into the high-frequency accelerating structure, if the laser pulse is synchronized to the correct RF phase for proper acceleration. Commercial lasers with the ability to synchronize themselves to external frequency sources became available in the same time frame. The electron source and accelerator functions can be combined into a single unit called a photocathode electron gun. A schematic of the photocathode electron gun of the Brookhaven National Laboratory Laser-Electron Accelerator Facility (LEAF) [6,14] is shown in **Figure 4** and a picture of the accelerator with the photocathode back plate removed is shown in **Figure 5**. While the LEAF accelerator consists of an integral structure of 3.5 microwave cavities that accelerates electron bunches to a final energy of 9 MeV when

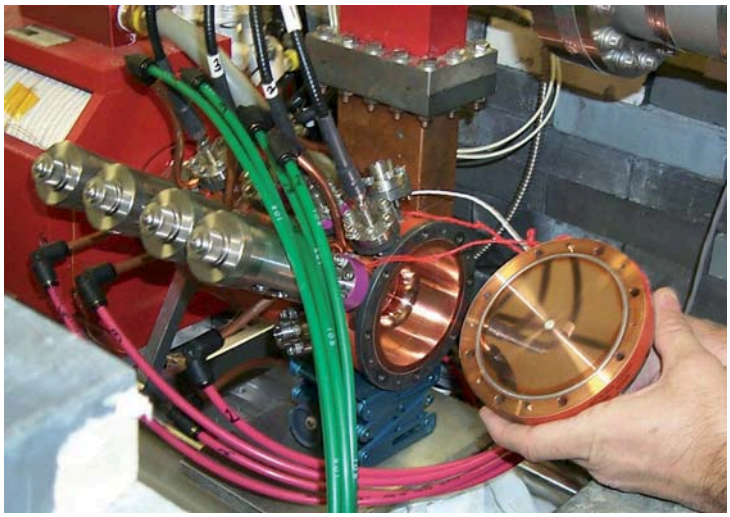

Figure 5 : *The LEAF accelerator opened to show the 6 mm diameter magnesium photocathode in the center of the back plate.*

driven with 15 MW of microwave power, 1.5 cavity photocathode electron guns that produce beam energies of 4-5 MeV are often used as injectors for systems with further accelerating stages, including most of the photocathode radiolysis facilities listed further below.

Photocathode-based picosecond electron accelerators are conceptually simpler than pre-bunched thermionic systems, although they require reasonably powerful, multicomponent femtosecond or picosecond laser systems to drive the photocathode. In addition, the availability of synchronized laser pulses allows the development of advanced detection capabilities with unprecedented time resolution. The combination of ease of use and powerful detection methods has stimulated strong interest in photocathode gun systems. Since the installation of the first photocathode electron gun pulse radiolysis system at BNL [5,13], four additional photocathode-based facilities have become operational and two more are in progress. The operational centers include the ELYSE facility at the Université de Paris-Sud XI in Orsay, France [7,8], NERL in Tokai-Mura, Japan [9,10], Osaka University [11,12], and Waseda University in Tokyo [13]. Facilities under development are located at the Technical University of Delft, the Netherlands, and the BARC in Mumbai, India.

The latest development in ultrafast electron sources for pulse radiolysis does away completely with accelerating structures. Instead, femtosecond laser pulses at terawatt power levels are focused tightly onto jets of helium atoms. The extremely strong electromagnetic field of the laser radiation strips the electrons off the helium atoms and accelerates them to very high energies, in a process called laser wake-field acceleration [25,26] but sometimes referred to as "Table-Top Terawatt" or T^3. Efforts are being made to characterize and control the energy spectrum of the accelerated electrons [26]. Experiments have shown that it is possible to use beams from these systems to do pulse radiolysis measurements [27], although energy spread of the electron beam and geometrical constraints place the practical time resolution in the few picosecond range despite the use of femtosecond laser pulses. Laser wake-field acceleration is studied in several laboratories around the world, but work on its development as a radiolysis method has occurred at the Terawatt Ultrafast High Field Facility at Argonne National Laboratory (**Fig. 6**) [28], the Laboratoire d'Optique Appliquée, École Polytechnique-ENSTA, Palaiseau, France [25-27], NERL in Tokai-Mura, Japan, and the Rutherford Appleton Laboratory in the UK. T^3 systems also hold promise as ultrafast X-ray sources.

Experimental Detection Techniques for Ultrafast Radiolysis

Transient absorption optical detection methods for picosecond and faster resolution are subject to a number of considerations. First, the velocities of high-energy electrons are approximately that of the speed of light in vacuum, $v_{elect} \approx c$, whereas light itself

is slowed by the refractive index n of the sample $v_{light} = c/n$. Therefore, visible light falls about one picosecond behind the electron beam for each millimeter of transit through water when the laser and electron beams are co-linear, thus the time resolution is constrained by the path length through the sample and must be traded off against signal magnitude. An arrangement that uses beams that cross at an angle can be used to compensate for the difference in velocities [31]. Another factor is that real-time, digitizer-based optical detection systems have response (bandwidth) limitations that limit time resolution, although technology has improved over the years. Still today, extremely fast biplanar phototube detectors and high-bandwidth oscilloscopes (≥ 6 GHz) offer resolution in the visible region down to approximately 80 picoseconds, but that is still slower than the capabilities of the accelerator to produce short electron pulses. Detectors in other wavelength regions are slower and have complex responses that must be deconvoluted from the kinetics.

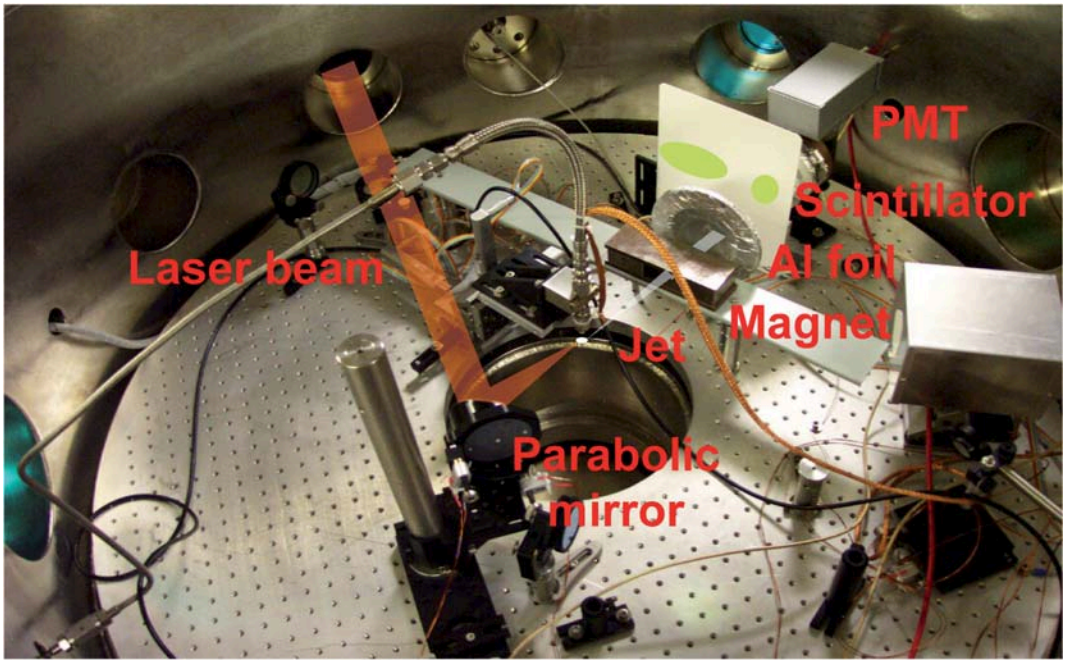

Figure 6 : *Vacuum chamber of the Terawatt Ultrafast High Field Facility (TUHFF) at ANL, configured for a measurement of electron beam energy dispersion (courtesy of R. Crowell).*

Another method of continuous detection is the use of a streak camera in absorption mode. Measuring radiation-induced emission with a streak camera is relatively straightforward, but sensitive transient absorption measurements are difficult to make because of limited dynamic range of the streak camera. The first work in this area was done in the 1970s, but little was done to follow up until the development of high-dynamic range

streak cameras in recent years. One such streak camera has been used to great effect to measure transient absorption spectra at the ELYSE facility in Orsay, France [8].

To overcome these limitations, stroboscopic detection methods have been used since the earliest picosecond radiolysis measurements (**Fig. 7**). Analogous to laser pump-probe experiments, in pulse-probe transient absorption spectroscopy a short pulse of light is used to measure the absorbance of a sample as a function of time delay between the electron pulse and the probe beam. Time resolution using this method is typically on the order of the electron pulse width. Originally, Čerenkov light generated from the electron beam itself was used as a variable-delay probe beam [1,2]. Later, a free-running Ti-Sapphire oscillator was used with a time-amplitude converter to measure spur decay of the solvated electron. With the advent of laser photocathode electron gun systems that provide picosecond-synchronized laser pulses, high-resolution pulse-probe kinetics measurements have nearly become routine. Timing improvements [12] and streak-camera jitter detection have made such measurements possible on thermionic, pre-bunched picosecond linacs as well. For transient spectroscopy, two methods of probe pulse generation are used to measure kinetics at wavelengths other than the fundamental of the gun-driving laser system (~ 800 nm). At some facilities, a white light continuum is generated by focusing intense laser pulses into a substrate such as a sapphire plate, fused silica or D_2O [10,11,13], while at others a specified probe wavelength is produced by an optical parametric amplifier pumped by the gun-driving laser system [6,12]. Broadband detection of the white-light probe is accomplished with a spectrograph/CCD or diode array combination [11], while single-wavelength detection is done with a pair of diodes [6,8,11,13]. Broadband detection works within the sensitivity range of silicon detectors (up to 950 nm), while NIR-sensitive photodiodes (Ge and InGaAs) extend the range of single-wavelength detection to 1700 nm. Pulse-probe transient spectroscopy has been used to follow the formation of Xe_2^* excimers in the radiolysis of supercritical xenon [29], measure dissociation rates of aryl halide radical anions, to re-evaluate the yield of hydrated electron at picosecond times [30], and to observe the solvation of excess electrons in ionic liquids.

While affording high time-resolution, pulse-probe absorption measurements typically require large numbers of shots to assemble a profile of the reaction by time and wavelength. Since cumulative radiation damage of the sample can be a problem, sample solutions are often flowed once-through or recirculated during experiments. Many interesting studies are thus not practical to perform because samples are not available in the necessary quantities or they cannot be flowed. To address this problem, techniques to measure complete time profiles or spectra, in one shot or just a few shots, have recently been developed. A group at ANL employed the Frequency-Domain Single Shot (FDSS)

spectroscopy technique where a high-bandwidth femtosecond pulse is stretched to several hundred picoseconds, passed through the sample, then dispersed by a monochromator onto a photodiode array, where each wavelength corresponds to a different time. The Osaka group has obtained spectra with high signal-to-noise in a single-shot, using a CCD to detect broadband absorption by reducing the time interval between sample and reference shots to 1 ms [11]. At BNL's LEAF facility, an optical fiber bundle is being used to create imaged probe beams containing 100 different time delays in a single shot.

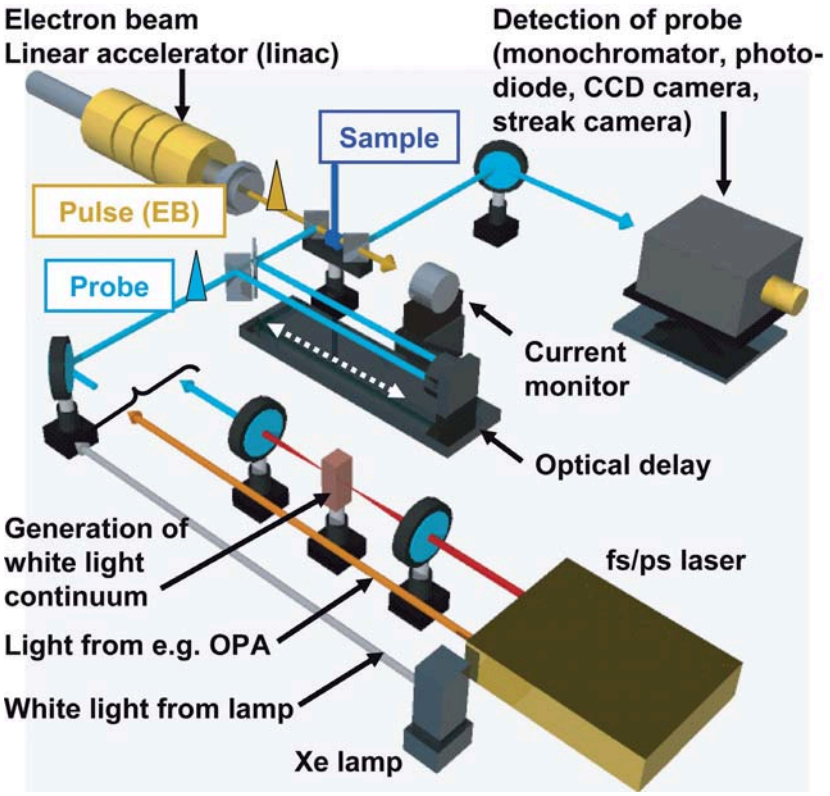

Figure 7 : *Schematic of a general detection system for picosecond pulse radiolysis (courtesy of Dr. A. Saeki, Osaka University).*

Heavy ion sources

Radiolysis experiments using heavy ion beams (protons and heavier atomic nuclei stripped of all electrons) occupy an important role, despite the relatively small number of investigators in this area. Because heavy ions have much higher LET values, the pattern of energy deposition, or track structure, is much denser than with "lighter" radiations. The variation of yields of radiolytic products as a function of LET, and the effects of variable

concentrations of scavengers on those yields, have provided critical information for the understanding of the radiolytic process [14,17]. The high local density of ionizations produced by heavy ions creates localized areas of damage that can be useful, as in the ion beam modification of polymers [14]. Ion beams have been used to fragment polymers to form membranes, and conversely, to polymerize precursor substrates to form forests of polymer rods on surfaces. The localized damage caused by heavy ions has important implications for radiation biology and radiation medicine. The American space agency NASA has established a heavy ion radiolysis facility at BNL (the NASA Space Radiation Laboratory) for *in vitro* and *in vivo* studies to prolonged exposure to heavy ion radiation in interplanetary space. Proton radiotherapy is a precise way of delivering large radiation doses to kill tumors. Heavy ion radiolysis of water produces the hydroperoxyl radical $HO_2^{\bullet}$, which is not formed by low-LET radiolysis in the absence of molecular oxygen. It is an important means of causing oxidative damage to hypoxic tumors.

Generally, heavy ion radiolysis experiments are performed at large, multipurpose accelerator facilities using cyclotrons or tandem Van de Graaff accelerators. The *Grand accélérateur national d'ions lourds* (GANIL) in Caen is the primary facility in France for heavy ion experiments. Major facilities in Japan include TIARA at the Japan Atomic Energy Agency, the Heavy Ion Medical Accelerator (HIMAC) in Chiba, and the High-fluence Irradiation Facility of the University of Tokyo. Heavy ion sources in the U.S. include ATLAS at ANL, the National Superconducting Cyclotron Laboratory at Michigan State University, and the Triple Ion Irradiation Laboratory at Oak Ridge National Laboratory. Because heavy ions are stopped in very short distances within samples, special techniques and equipment configurations are used to optimize transient signals.

Future trends

The past decade has been an encouraging period in the development of radiolysis capabilities that has reversed an earlier trend of decline in number and accessibility. Two new technologies, photocathode electron guns and laser wake-field accelerators, have emerged and spawned a large new generation of ultrafast accelerator facilities. These installations are developing advanced experimental techniques and making sophisticated experiments available to a larger community of researchers than ever before. Earlier-generation picosecond accelerators have been upgraded to high levels of performance. New nanosecond linacs were installed at Notre Dame, Saclay and Pune, and the University of Manchester has founded a program and Chair in Radiation Chemistry that will reinforce a field that was in danger of disappearing from the U.K. These developments attest to the fact that major research support establishments in several countries recognize that radiation

chemistry and radiolysis experimentation have important roles to play in solving future energy needs in many areas (including nuclear, solar and high-performance materials) and in developing science to protect human health and the environment.

It is not taking a risk to predict that performance and capabilities of the new radiolysis installations will markedly improve as these young facilities mature. But what other developments can we look forward to? Certainly there is strong interest in bringing additional spectroscopic tools into the pulse radiolysis laboratory. Efforts are underway to adapt transient mid-infrared detection techniques to pulse radiolysis, to take advantage of the specificity of vibrational spectroscopy [24]. Strong interest in nanoscience and the mechanisms of reactions in heterogeneous systems will push the development of interface-specific spectroscopies in radiation chemistry, for example surface-enhanced Raman spectroscopy and second-harmonic or sum-frequency generation.

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