Oct. 20, 1970 E. J. HART ET AL 3,535,087

DEVICE FOR PRODUCING AND MONITORING HYDRATED ELECTRONS

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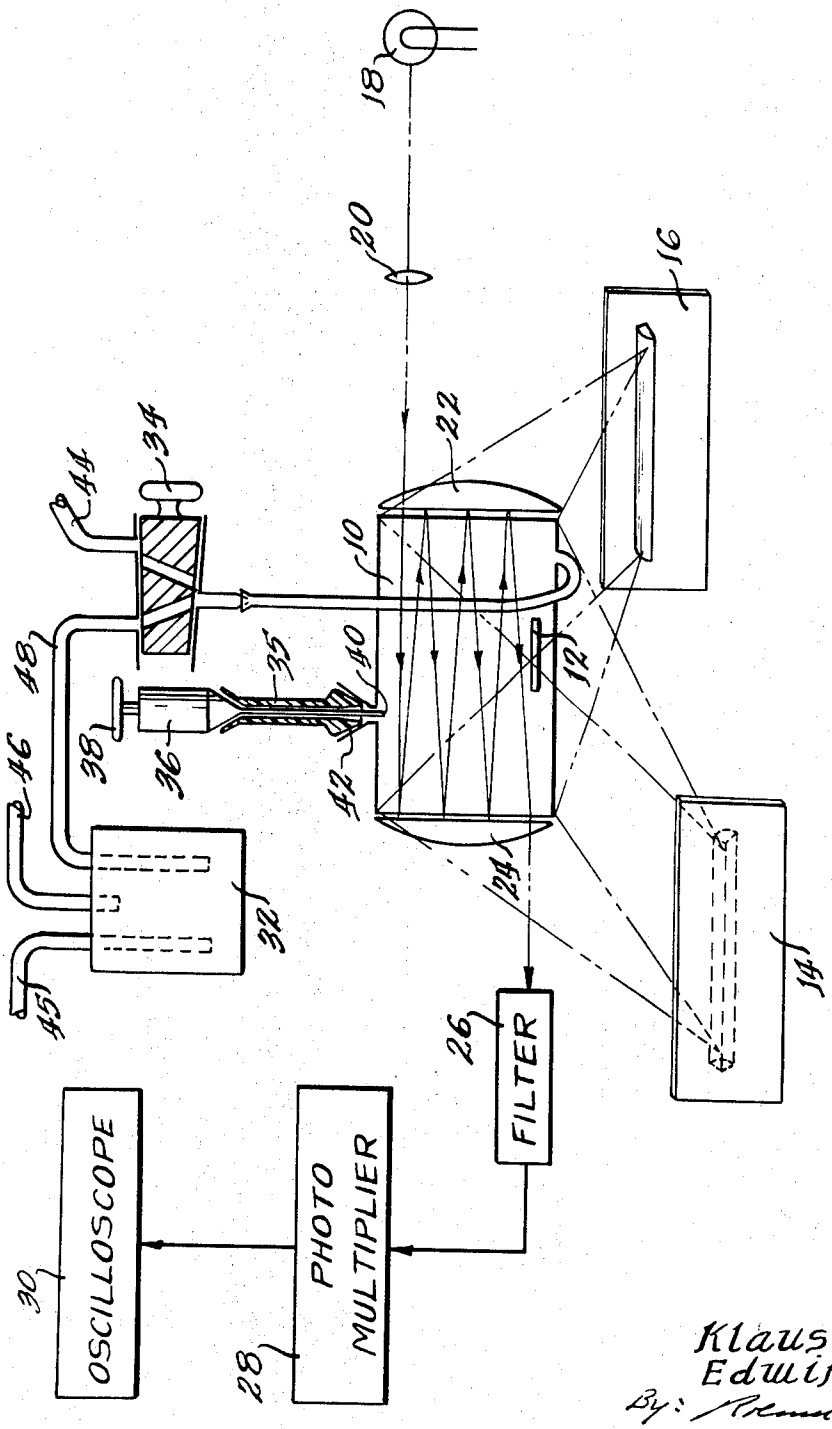


Fig. 1

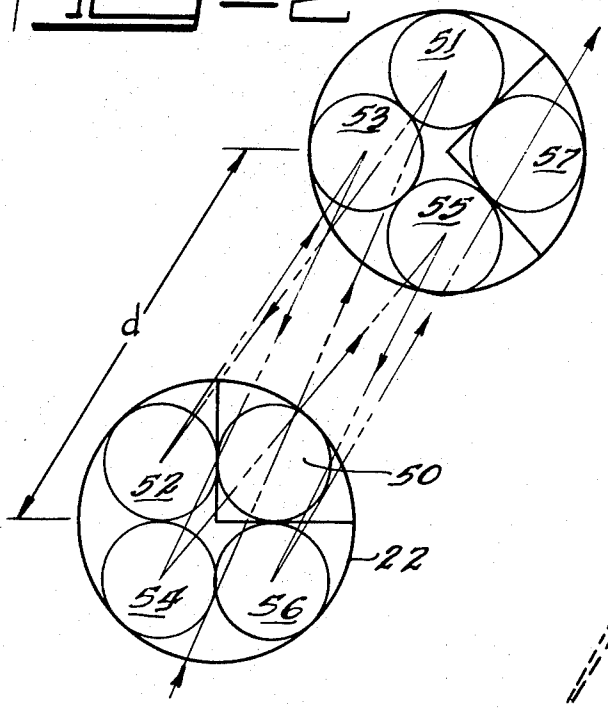
Inventors
Klaus H. Schmidt
Edwin J. Hart
By: Alvin A. Gutierrez
Attorney

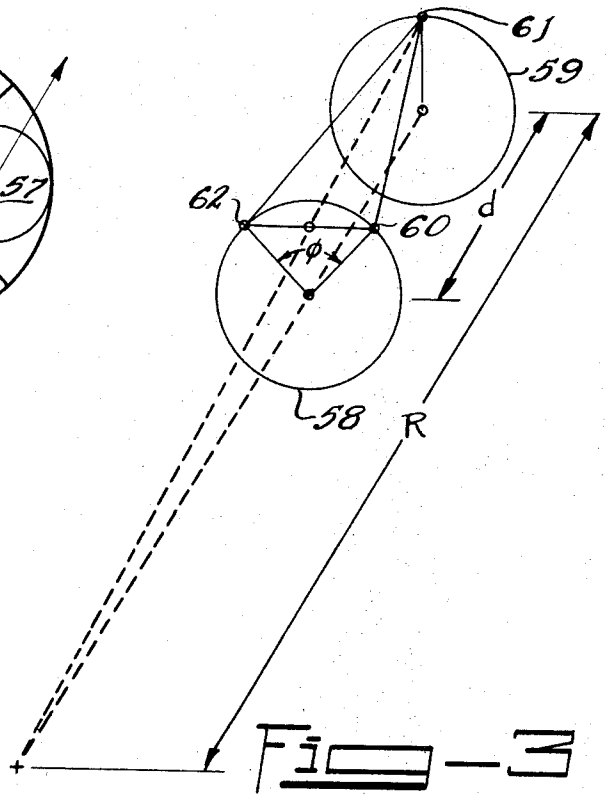
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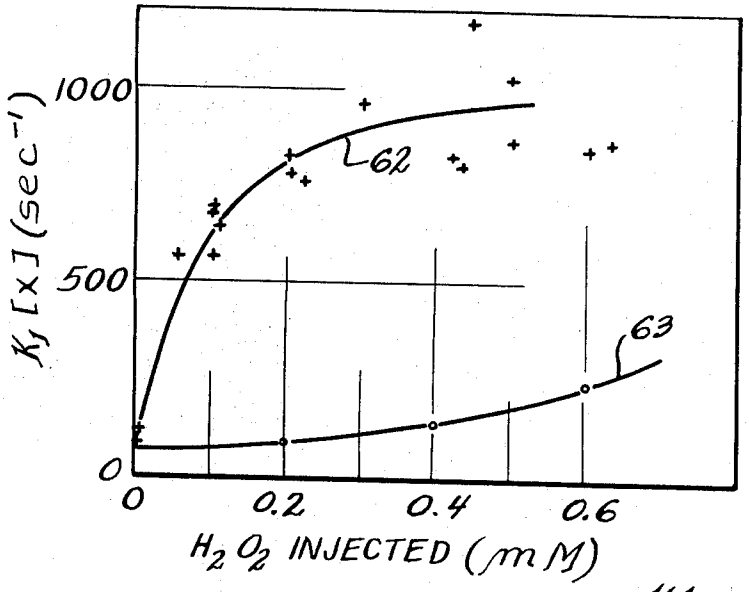
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Fig—2





Fig—3



Fig—4

Inventors
Klaus H. Schmidt
Edwin J. Hart
By: Edward A. Gutkowski
Attorney

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DEVICE FOR PRODUCING AND MONITORING HYDRATED ELECTRONS

Edwin J. Hart, Hinsdale, and Klaus H. Schmidt, Downers Grove, Ill., assignors to the United States of America as represented by the United States Atomic Energy Commission

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Int. Cl. G01m 21/34, 27/00, 33/18
U.S. Cl. 23—253 5 Claims

ABSTRACT OF THE DISCLOSURE

A relatively simple photolytic device for producing and detecting hydrated electrons in sufficient quantities and with adequate sensitivity to be useful for demonstration, research and analytical purposes. Also a spherical mirror arrangement which increases the sensitivity of the detection system, permitting smaller quantities of hydrated electrons to be analyzed than would otherwise be possible.

CONTRACTUAL ORIGIN OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

BACKGROUND OF THE INVENTION

The hydrated electron (e_{aq}^-)—which is a higly reactive negative ion—has broad uses in chemistry because of its unique properties. In water it is a more powerful reducing agent than the hydrogen atom by 0.6 volt. It is the dominant reducing species in irradiated water and many radiolytic mechanisms have been explained once the rate constants for the hydrated electron were established.

Because of the power of the hydrated electron as a reducing agent, it is useful in certain types of analytical work. For example, it is extremely useful and accurate in determining minute amounts of oxygen and other reducible substances present in water. A method for using hydrated electrons as an analytical tool in determining concentrations of reducible substances in aqueous solutions is the subject of assignee's U.S. patent application Ser. No. 547,032, now U.S. Pat. No. 3,429,667, filed May 2, 1966.

A major drawback in the utilization of the hydrated electron as a research and analytical tool is that producing or generating the hydrated electrons has required the use of electron accelerators or high-level X-ray or γ-ray sources. Not only are such sources dangerous to operate and difficult to use, but they are limited in number and not readily available for general use.

Recently it was discovered that hydrated electrons may be generated by a flash of ultraviolet radiation directed into a proper aqueous solution and it is the object of this invention to provide such a device which is safe, easy to use and relatively inexpensive and which may be used as a demonstration device and yet is sufficiently sensitive to be used as a research or analytical tool.

SUMMARY OF THE INVENTION

We have developed a compact, safe and reasonably inpensive device which utilizes the principle of flash photolysis. Our device makes the hydrated electron readily available to all who would want to use it, either for demonstration purposes or as a research or analytical tool. It is capable of producing up to 10^{-7} M e_{aq}^- in a single 40 μsec. light pulse and is capable of detecting less than 10^{-9} M e_{aq}^-.

The device of this invention contains a hydrated electron generation portion and a hydrated electron detection portion. The generation portion consists of a cell containing a matrix solution within which the electrons are generated, a mercury vapor light for preirradiating the solution for removal of undesired substances which react with the hydrated electron and which may be present therein and a xenon flash lamp for generating the hydrated electrons in the matrix. The detection portion contains a tungsten detection light source, a spherical mirror system for passing the detection light through the matrix a number of times, a light filter for selecting light of the wavelength which is best absorbed by the hydrated electrons, a photomultiplier for detecting decreases in light transmission and generating a corresponding signal, and a readout device for displaying the signal, such as an oscilloscope.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram of apparatus forming the subject matter of this invention.

FIG. 2 is a diagram which is designed to clarify the way in which the beam is reflected back and forth between the mirrors.

FIG. 3 is a diagram of the geometrical relationship of the mirror system of this invention.

FIG. 4 is a chart showing plots of results obtained with various concentrations of H_2O_2 designed to show reproducibility of results obtainable with this device.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As shown in FIG. 1, the apparatus includes a quartz radiation cell **10** having opposite ends which are flat and parallel to each other. Cell **10** is provided with a stirrer **12** which a glass-encased iron rod actuated by a solenoid which receives repetition pulses of about two cycles per second from a pulse-generating circuit which is not shown. Cell **10**, after introducing a matrix solution thereinto, is irradiated by ultraviolet light from mercury lamp **16** and by flashes of ultraviolet light from xenon lamp **14**. Light from tungsten lamp **18** is focused by lens **20** through a first plano-convex mirror **22** onto a second plano-convex mirror **24**, one mirror being located at each end of cell **10** and having its plano face in contact with the flat surface of the cell and each mirror having one 90° sector transparent to permit passage of light therethrough. Seven passes of light through the cell are employed to increase sensitivity of the detection method. For the final pass, the light is reflected by mirror **22** through mirror **24** and through a wide band pass filter **26**. The light from the selected wavelength range is then passed into a photomultiplier tube **28**, the signal from which is displayed on an oscilloscope **30**.

The matrix solution is introduced into cell **10** from a mixing vessel **32** through line **48** and through a two-way stopcock **34**. The sample is introduced into cell **10** by means of microsyringe **36**, provided with plunger **38** and having a long glass capillary **40**, syringe **36** being inserted into injection receptacle **35** which is in turn connected to cell **10** through joint **42**. Cell **10** is emptied by disconnecting microsyringe **36** and substituting an inert gas line connected to injection receptacle **35**. Two-way stopcock **34** is turned to connect waste line **44** to cell **10** and the matrix solution in cell **10** is blown from cell **10** by the inert gas.

Cell **10** is made from quartz having the best possible transmissibility of ultraviolet light. Although cell size is not critical, the cell used in the present apparatus has an outer diameter of 25 mm. and an over-all length of 52 mm.

The matrix solution is a 10^{-3} M NaOH solution having a pH of 10–11 which has been saturated with hydrogen. The matrix is prepared by filling container **32** with triple

distilled water and bubbling hydrogen through line **45** into the water for about two minutes in order to remove the bulk of air and CO_2. The hydrogen exhausts through line **46**. Then 0.1 M NaOH solution is added to the water and hydrogen is again bubbled through the solution for 15 minutes to saturate the solution. The cell is first flushed with hydrogen gas, then the hydrogen saturated solution is forced into the cell through line **48**. This solution is forced from the cell through waste line **44** and the cell is again filled with matrix as before. After this preparation, the matrix solution is less than 10^{-6} M in oxygen.

The pH of the matrix solution is critical, since it is only an an alkaline solution containing hydrogen that the hydrated electron exists long enough to be useful. At a pH of below 10, insufficient OH^- ions are present in the solution to convert H^+ atoms to hydrated electrons which is an important secondary reaction for the formation of hydrated electrons. Above pH 11, the effective ultraviolet light will not penetrate the cell far enough because of the increased hydroxyl ion concentration.

Hydrated electron decay curves obtained immediately after filling the cell with matrix solution have small amplitudes and half-lives of only a few tenths of a millisecond. This is due to impurities, particularly oxygen, which react rapidly with the hydrated electrons. In order to remove this trace of oxygen, the matrix is irradiated with ultraviolet light from mercury lamp **16** This procedure effectively removes oxygen from the solution by producing small quantities of hydrated electrons which neutralize any oxygen or other scavengers which may be present. After preirradiation, e_{aq}^- signals are obtained with considerably larger ampltudes and longer half-lives. This preirradiation may continue for about two minutes, or until a constant decay of e_{aq}^- results—typically with a half-life of 5–8 milliseconds (msec.) Irradiation of the matrix may be accomplished either before the intermittent radiation, i.e. before the flash photolysis takes place, or during the flash radiation without affecting the results.

After cleanup, up to 1 ml. of sample scavengers, such as hydrogen peroxide in submicromolar amounts, are introduced into the matrix in cell **10** by microsyringe **36** while stirring the matrix by means of stirrer **12**. The sample solution is hydrogen-saturated in the same manner as the matrix solution. After a thorough flushing with sample solution, the syringe is filled and inserted into injection receptacle **35** attached to cell **10** by joint **42**. The lengths of syringe **36** and capillary **40** are adjusted so that the tip of the capillary protrudes about 1 mm. into the cell. In this way the sample solution is injected directly into the matrix, thus insuring a virtually air-free filling.

The hydrated electrons are generated in the matrix by subjecting the solution to a flash of ultraviolet light from xenon lamp **14**, resulting in the following reactions:

$$OH^- + h\upsilon \rightarrow OH + e_{aq}^-$$
$$OH + H_2 \rightarrow H_2O + H$$
$$H + OH^- \rightarrow e_{aq}^-$$

Each light quantum effective in the first reaction eventually produces additional hydrated electrons by the reactions represented by the second and third lines above. These reactions greatly increase the quantities of hydrated electrons which may be generated by a given flash of light.

Both mercury lamp **16** and xenon lamp **14** are mounted in cylindrical stainless steel reflectors which have been polished and vacuum-coated with aluminum to improve reflectivity. The distance that the xenon lamp is placed from the matrix-filled cell is dependent upon the quantities of hydrated electrons desired, the type of reaction which is under study and the efficiency of the reflector surrounding the lamp. Thus, if large quantities of hydrated electrons are wanted, placement of the flash lamp only several inches from the cell is necessary to produce the desired results. However, if smaller quantities of electrons are sufficient, then a lamp-to-cell distance of 6–8 inches would be quite adequate.

The presence of the hydrated electron in the matrix and its decay are detected by passing a beam of light through the matrix. The hydrated electrons in the matrix strongly absorb light in the region of 7200 A. and the change in the intensity of the light is monitored by a band pass filter, photomultiplier tube and oscilloscope combination. Lamp **18** is a tungsten iodide lamp providing a point source of light to simplify focusing the light beam by lens **20** through first mirror **22** and through cell **10** onto mirror **24**.

Mirrors **22** and **24** are plano-convex lenses made of Pyrex on which the convex sides have been silvered to reflect the light beam except for a 90° section through which the entering and exit light beam passes.

Referring now to FIG. 2, the beam of light is focused by lens **20** so that the lamp filament is focused in about the center of cell **10**. The beam passes through mirror **22** at sector **50** and is reflected at sector **51** on mirror back **24** to sector **52** on mirror **22**. The beam of light is reflected from sector to sector around an axis joining the centers of mirrors **22** and **24** until the beam of light passes through mirror **24** at transparent sector **57**. By this mirror arrangement, the light rays which make up the beam remain generally parallel and the cross section of the beam of light may be adjusted so that the beam fills a maximum of each sector. Because the cross section of the light beam passing through the cell is greater than that possible with other mirror systems, light of greater intensity is able to reach the photomultiplier tube, increasing the signal-to-noise ratio and improving the hydrated electron detection sensitivity.

In FIG. 3, circles **58** and **59** represent the locus of points of reflection for the center of the light beam as it is reflected by mirrors **22** and **24**, respectively. The figure shows the geometrical conditions for reflecting a light beam from point **60** on circle **58** to point **61** on circle **59** and back to point **62** on circle **58** in such a way that the desired value for the angle ϕ is established. This is established by defining the radius of curvature (R) for the mirror surfaces of mirrors **22** and **24** by the formula:

$$R = \frac{d}{1 - \cos\frac{\phi}{2}}$$

where d is the distance between mirrors and $\phi/2$ is the angle of rotation per reflection. Thus, the radius of curvature of the mirrors must be 3.414 times their distance apart when ϕ is 90°.

In FIG. 1, mirrors **22** and **24** are shown positioned with their flat surfaces adjacent to the flat ends of cell **10**. This requires that a refractive correction be made for the glass used. By using either water or oil immersion between the mirrors and cell, total light transmission improved by about 80–100%.

The wide band pass filter is a conventional filter of about 200 nanometers (nm.) wide in the region of 700 nm., which is the absorption spectrum of the hydrated electron. The photomultiplier and oscilloscope are also conventional. The photomultiplier used is of the S–1 response type having an end window such as an RCA 7102 and its associated power supply. Any D.C. oscilloscope with a minimum sensitivity of 10 mv./cm. and a rise time of as much as 5 μsec. will be adequate, provided it will not overload so that the response will remain linear to prevent overshoot. A Tektronix type 564 storage oscilloscope with a 2A63 plug-in amplifier and a 2B76 time base proved to be satisfactory for use in the apparatus.

A series of experiments were run to study the mechanism of the H_2 and H_2O_2 reaction and to ascertain the ability of the apparatus to reproduce results. This was done by injecting various amounts of 20 μM H_2O_2 into the matrix. Up to 1 ml. of the H_2O_2 stock solution was injected in volumes of 0.1 or 0.05 ml. and the oscilloscope

trace recorded after each addition. After the first 0.5 ml. had been injected, the cell with the syringe in place was irradiated with the mercury lamp to bring the decay curve back to its original shape. Next a second series of injections were made using the remaining 0.5 ml. of the stock solution in the same way. In FIG. 4, the first-order component, $k[H_2O_2]$ of the decay curves is plotted vs. the initial H_2O_2 concentration. Line **62** is the average of H_2O_2 plots, while line **63** shows the effect of injecting various quantities of hydrogen-saturated water into the matrix as a control. As can be seen by the plots along line **62**, excellent reproducibility of results may be obtained with the present invention.

It will be understood that the invention is not to be limited by the details given herein but that it may be modified within the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A device comprising:

(A) hydrated-electron-producing means consisting of:
- (a) a quartz cell containing a hydrogen-saturated alkaline solution,
- (b) a steady ultraviolet light from preirradiating said solution,
- (c) an intense ultraviolet light periodically irradiating said solution, thereby producing detectable quantities of hydrated electrons therein; and

(B) hydrated-electron-detection means consisting of:
- (a) a source of detection light,
- (b) a pair of spherical reflectors for directing said light through said solution a plurality of times, each said reflector having a portion of its surface transparent for the passage of light therethrough, the intensity of said light being diminished in direct proportion to the quantity of hydrated electrons present in said solution,
- (c) means for filtering said light and passing only light of a preselected wavelength range,
- (d) a photomultiplier tube to sense said selected light and generate a singal in response to changes of intensity therein, and
- (e) means for displaying said signal.

2. The device of claim **1** wherein the hydrogen-saturated alkaline solution is a dilute NaOH solution having a pH of 10–11.

3. The device of claim **2** wherein the quartz cell has two flat ends which are opposite and parallel and the spherical reflectors are plano-convex lenses, said plano surface being immediately adjacent each said flat end of said cell, said convex surfaces being reflectorized except for a small portion to permit the passage of light therethrough, and wherein the radius of curvature (R) of the convex surfaces is equal to

$$\frac{d}{1-\cos\frac{\phi}{2}}$$

where d is the distance between the convex surfaces and $\phi/2$ is the angle of rotation per reflection.

4. The device of claim **3** wherein the steady ultraviolet light is a mercury lamp, the intense ultraviolet light is a xenon capillary flash tube and the detection light is a tungsten iodide lamp.

5. The device of claim **4** wherein the means for filtering said light is a band pass filter set to pass light of about 700 nanometers and said display means is an oscilloscope.

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MORRIS O. WOLK, Primary Examiner

ELLIOTT A. KATZ, Assistant Examiner

U.S. Cl. X.R.

204—193; 250—43, 218