RADIATION LITMUS PAPER

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SUMMARY
We have developed a colorimetric method for measuring doses of ionizing radiation at low (10^{-4}-10^{-2} Gy) levels. This method uses photographic film as the sensor and amplification method, coupled with developers that are extremely non-fogging and tolerant of acidic conditions, and a pH indicator. The reaction is packaged so that the film can remain unactivated by ambient light while the developer and pH indicator can migrate to a viewing window. The result is a self-developing film badge that provides real-time dose information. This device, called Radiation Litmus Paper (Figure 1), is modeled after the M256A1 Chemical Test Kit (Figure 2) which is manufactured by Anachemia and used by the US military as well as state and local first responders.

Figure 1. Field prototype of Radiation Litmus Paper.

I. BACKGROUND

Colorimetric radiation dosimetry has historically been limited to high dose measurements. Examples include the liquid-phase US Army Tactical Dosimeter, which measures doses from 0.5 Gy to 4.5 Gy; liquid phase Fricke dosimeters that measure approximately from 10 Gy to 500 Gy; and several solid phase systems intended for measuring food irradiation efficiencies.

Low dose colorimetric measurement is difficult to achieve because of the large difference between the number of molecules of a colorant that may be produced by, for example, a 0.1 Gy radiation dose and the number of molecules needed for observation by the human eye. This difference is often a factor of 10^4-10^5. This gap can be partially bridged by using halocarbons as radical chain carriers, but realistic efficiencies of these chain reactions is only a factor of 10-100.

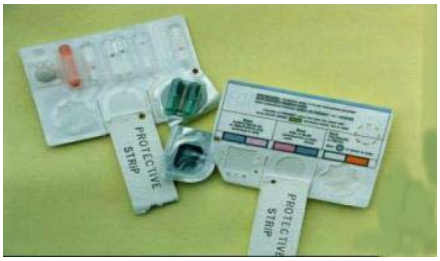

Figure 2. Anachemia M256A1 Chemical Test Kit.

II. APPROACH

Amplifications significantly greater than those provided by halocarbons are required to allow a colorimetric dosimeter that measures doses on the order of 10^{-4} Gy. Photographic film provides the required amplification as well as the required environmental stability. However, film is sensitive to light, and therefore cannot be directly observed without contaminating the results. The reactions that govern photography and radiography are shown in equations 1-5.

$(AgBr)_{n+m} + RH \rightarrow$ no reaction (1)

$(AgBr)_{n+m} + RH + time \rightarrow$ fogging (2)

$(AgBr)_{n+m} + radiation \rightarrow (AgBr)_n Ag_m + Br^{\bullet}$ (3)

$(AgBr)_n Ag_m + RH \rightarrow Ag_{n+m} + HBr + R$ (4)

$$Base + HBr \rightarrow BaseH^+ + Br^- \quad (5)$$

Equations 1 and 2 describe the reaction between unexposed film and developer. Equation 1 shows the desired lack of reaction between unexposed film [$(AgBr)_{n+m}$] and a developer [RH]. Typically, n is 10^7-10^9 and m at least 4. Unwanted fogging, which is the thermally activated reduction of silver bromide by a developer, will occur in time, as shown in equation 2.

Equation 3 describes the reaction of a grain of silver bromide with light or ionizing radiation. A small amount of Ag(I) is photoreduced to Ag(0), and the corresponding (but inconsequential from a chemistry perspective) amount of bromine reacts with the gelatin matrix.

In equation 4, the photoreduced silver forms a catalytic spot [Ag_m] on the grain of film [$(AgBr)_n$] that promotes the reaction of the grain of silver bromide and the developer. The products of the reaction are the oxidized form of the developer [R] and acid [HBr].

The acid is reacted with a base, as shown in equation 5. This step is required for most developers, because their activity is seriously attenuated by acid.

Equation 4 forms the basis of photographic images. The reduced silver is used in black-and-white photographs, and the oxidized developer can be reacted to form dyes for color photography. To use these reactions for real-time radiation dosimetry, we had to modify several of the reactions described above. Equation 2 had to be dramatically suppressed, so that it occurred only after tens of hours rather than several minutes. Equation 4 offered a possible colorimetric signal, if the developer changed color when it was oxidized and did not become anchored into the gelatin matrix. The acid-base reaction in equation 5 also offered a colorimetric signal if the base were a pH indicator.

Our approach, therefore, was to design a system where the film would be kept in a light-proof container with a channel that allowed a solution of pH indicator and developer to contact it. The developer/pH indicator solution would be kept in a transparent container, so that the extent of the reaction could be monitored by simple visual inspection. Liquid-phase reagents (developer, pH indicator) and products (oxidized developer, protonated pH indicator) could travel back and forth between the transparent and opaque portions of the dosimeter, while solid-phase materials (film, reduced silver) could not.

The principal chemistry research that was required was to design a developer that did not lead to rapid fogging (equation 2), that was active at neutral pH levels (to allow maximum sensitivity), and that changed color when oxidized. Fe(II) coordination compounds offered these properties.

III. MEASURED DATA

Devices were constructed using Kodak NTB-2 or NTB-3 autoradiography gel as the film source. A solution of Fe(II)EGTA and a pH indicator (typically phenol red, although many indicators worked), with the pH adjusted to just basic of the indicator point. The devices were irradiated with a 5 mCi ^{137}Cs source, and visually examined periodically until the color was judged to have unambiguously changed from red to yellow. The devices also provided intermediate colors that corresponded to measurements of lower doses, but we wanted to avoid the need for fine judgement calls in general. The dosimeter was also tested with AmBe neutrons and ^{90}Sr beta radiation, although no calibrations were performed.

Several factors could control the performance of a Radiation Litmus Paper device. These factors include the volume of the developer/pH indicator solution, the concentration of the pH indicator, the surface area of the film, and the film speed.

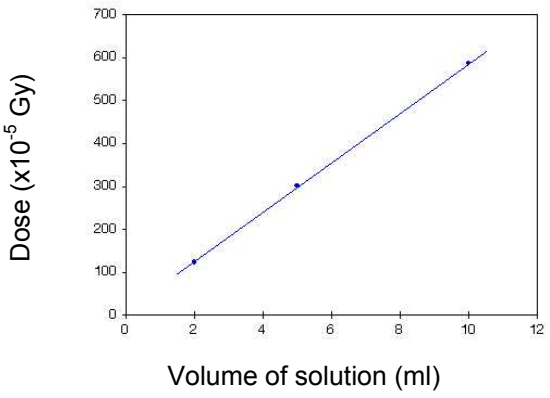

Figure 3. Sensitivity of Radiation Litmus Paper as a function of the volume of the developer/pH indicator solution.

Figure 3 shows the effect of changing the volume of the developer/indicator solution. These tests

were carried out with 0.3 mL of Kodak NTB-3 autoradiography gel with a surface area of 2.27 cm^2. An Fe(II)(EGTA) developer solution with phenol red pH indicator was used. The sensitivity of the devices varied inversely with the volume. The reason for this behavior is that the color changes with acid concentration. Acid is generated by the reactions listed above in equation 4. By varying the amount of water in which the acid is dissolved, we could control the change in pH.

Figure 4 shows the dependence of the devices on the surface area of the silver bromide emulsion. This curve consists of data from devices made with Kodak NTB-3 autoradiography gel (varying amounts), 5 mL of a Fe(II)EDTA/phenol red solution made with a higher concentration of phenol red (upper line) and a lower concentration of phenol red (lower line). This curve shows several dependencies.

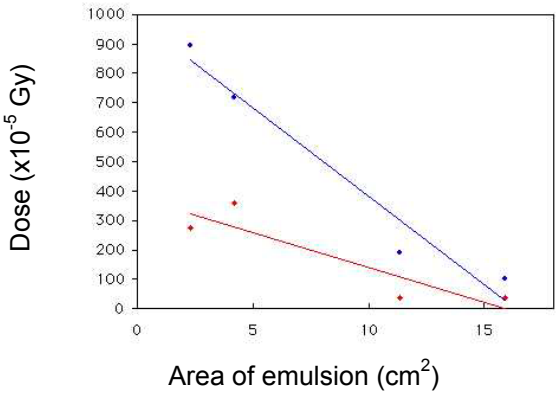

Figure 4. Sensitivity of Radiation Litmus Paper as a function of the area of the silver bromide emulsion and as a function of the pH indicator concentration.

The first dependence is that of the device sensitivity on the surface area of the silver bromide emulsion. A larger sensor clearly will collect more radiation than a smaller one. Capture efficiency is low, and therefore one might expect that the volume of silver bromide would be proportional to surface area. This is not, however, the case. Experimentally, we determined that the sensitivity varied unpredictably with the volume of the silver bromide emulsion at low volumes, but became invariant at higher volumes. By dismantling devices, we found that at low emulsion volumes, our surface areas were irreproducible. At higher silver bromide emulsion volumes we did completely cover the intended areas. However, the developer would only penetrate a small distance into the silver bromide emulsion. We therefore found that the volume of silver bromide that had any effect was determined by the surface area (which we could control) times the developer penetration depth (which we could not affect). We therefore decided to report surface area. We found that we could increase sensitivity by placing channels in the silver bromide emulsion, which allowed greater developer penetration. However, these channels were difficult to reproduce reliably.

The second dependence shown in figure 4 is on indicator concentration. Higher indicator concentrations make the color change more intense, but require more acid to protonate the indicator. Lower indicator concentrations make the color change more faint, but allow for more sensitive devices.

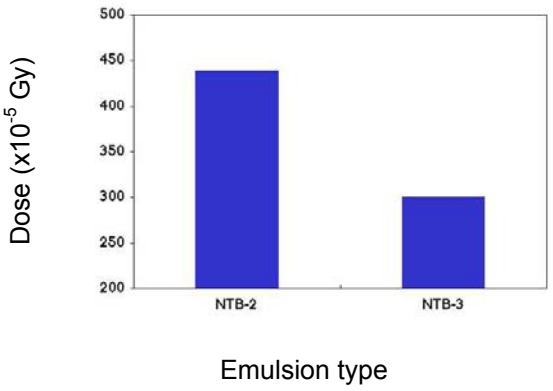

Figure 5. Sensitivity of Radiation Litmus Paper as a function of the area of the silver bromide emulsion and as a function of the pH indicator concentration.

Figure 5 shows the dependence of the devices on the grain size of the silver bromide. These experiments were carried out with 2.27 cm^2 surface area of Kodak NTB-2 and NTB-3 autoradiography emulsion, and 5 mL of Fe(II)(EGTA) developer with dilute phenol red indicator. NTB-2 has an average silver bromide grain size of 0.26 microns, and NTB-3 has an average silver bromide grain size of 0.34 microns. Both grain sizes only require 3-4 atoms of metallic silver to become activated, but the larger NTB-3 grains have approximately 2.2 times the silver bromide. Experimentally, the NTB-2 devices were 1.5 time less sensitive than the NTB-3.

IV. PROBLEMS

The principal problem we encountered was the difficulty of making Radiation Litmus Paper devices for testing. The devices were time-consuming to build, because they had to be constructed by hand in a darkroom. We constructed them typically 20 at a time. The principal difficulty was that if there were a light leak, the device would register a false positive. Light leaks could be discerned by destructively examining the emulsion after a device was tested. A functional device would show an even pattern of developed silver, while a light leak would produce a spot or stripe of heavily developed silver in an otherwise undeveloped emulsion. We believe that these problems are solely a function of hand construction, and that Radiation Litmus Paper is ready for mass production.

V. CONCLUSIONS

By using well-established film chemistry to provide the amplification needed to see a low dose of ionizing radiation, we were able to construct the first low dose colorimetric method for measuring ionizing radiation. Radiation Litmus Paper is intended to function as a simple method for ascertaining possible danger from ionizing radiation for "first responders." It is intended to operate similar to the M256A1 chemical test kit currently used by the US military as well as state and local officials.

ACKNOWLEDGMENTS

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