Studies on Radiation Dosimetry by a Solid Color Changing Substance
(Solid Color Radiation Dosimetry)*

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ABSTRACT

A study on the solid chemical dosimeter was made to improve the sensitivity to x-ray and the stability to ultraviolet ray. According to the results obtained with gelatin, cellulose, plastic, paraffin and fat, the best material as a base was as paraffin. The small amount of vaseline was added into paraffin to prevent the crack and flake forming.

The results of the screening of about 100 dyes showed that methyl yellow was the best dye of those to detect the effect of x-ray irradiation in chloroform-paraffin system. Dithizone was sensitive dye in carbon tetrachloride-paraffin system.

Many kinds of organic or inorganic compounds were blended into the chloroform-paraffin-vaseline system to sensitive the response to ionizing radiation and stabilize to ultraviolet ray. Para-hydroxyazo benzene was most effective as a sensitizer and stabilizer. Several halogenated hydrocarbons were mixed into the methyl yellow-paraffin-vaseline system to check the degree of color change produced by x-ray

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irradiation, and it was found that chloroform was the best of these for methyl yellow system.

From these experiments, the practical dosimeter was made by mixing of methyl yellow, p-hydroxy azo benzene, paraffin and vaseline. Three methods with electric, optical and pH meter were tried in order to measure the amount of chemical products in the dosimeter, but the measurement with pH meter was most applicable. The amount of acid produced by x-ray irradiation was directly proportional to the exposure dose up to 5000 r. The multi color changes proportional to changed dose were made by the combination of dithizon and methyl yellow added into carbon-tetrachloride-chloroform mixture.

INTRODUCTION

A solid substance which will absorb ionizing radiation to a degree equal to that of living tissue is sought after. Such a substance would facilitate detection and measurements of the dose of radiation and would also contribute to basic radiology and to various clinical fields.

Recently attention has been drawn to the studies which were made in this direction by M. S. Potsaid and G. Irie\(^{1,2}\). In their studies they made a solid block of a light yellow shade by mixing paraffin with methyl yellow and chloroform or bromoform. When exposed to ionizing radiations, this substance changed its color from light yellow to red and the degree of the color-change corresponds to the amount of ionizing radiations absorbed. These substances are called "paraffin base halogenated hydrocarbon chemical dosimeters" or "in-phantom radiation detectors".

Since the substances are mixtures obtained by adding pH indicators or other similar dyes and halogenated compounds to a paraffin base, they are approximately tissue-equivalent in respect to the elementary composition as well as specific density. The paraffin base has another advantage in that these mixtures can be moulded into the desired shape. The color changes are apparent to the naked eye even during irradiation. Colored x-ray pictures are also obtainable. One of the advantages of this solid is that its chemical purity is not so important as in the case of ordinary liquid chemical dosimeters\(^{3}\). The drawback of this solid is that the color fades markedly in 24 hours, and that no accurate method for measuring the absorbed dose has been devised.

The present report is concerned with some improvements obtained from further fundamental studies on the solid chemical dosimeters.

In view of the possible future work in this direction, we have included notes on work done hitherto, in hopes that repetition may be avoided.

EXPERIMENT

Exp. I. On the base material
1. water-soluble materials
   i) gelatin
ii) methyl cellulose
iii) sodium arginate

Experiments were made on the above bases to which water, chloroform and dye were added. Possibly due to the protective effect in radiation chemistry these substances showed a low sensitivity to x-rays. They were also difficult to mould because of their gel-like cohesiveness. Evaporation of water caused a low reproducibility and made it impossible to preserve the material for a length of time. The most disadvantageous characteristic was that the colored part were blurred presumably due to diffusion of the irradiation products. For these reasons, the substances mentioned above are ruled out for use as a base.

2. non-water-soluble materials
   i) polystyrol
   ii) polymethyl-meta-acrylate

Another series of experiments was performed on some plastic materials that are soluble in chloroform. When chloroform was added, these substances turned gel-like. And showed transparancy higher than that of substances with watersoluble bases mentioned in experiment 1.

The blurring in the colored portion was not as bad as in experiment 1. But the gel-like cohesiveness, the difficulty in moulding and low sensitivity to the radiations disqualified them as base material.

Still their high transparency was an advantage, and if these defects can be eliminated by using other halogenated compounds, they may be useful.

iii) fats

Tests were made to determine the suitability of lanolin and other fats as a base. In these substances the color faded so rapidly that further tests were discontinued.

iv) paraffins

When a proper amount of chloroform is added, paraffin which M.S. Potsaid and G. Irie used in their experiments, was found to be the most suitable base known up to date. It has no cohesiveness and is easy to mould. A slight blurring of colors which may be due to diffusion was seen. The defects in this material were low transparency and snow-shaped spots and cracks.

As a result of repeated tests it was ascertained that the best combination for eliminating the snow-shaped spots and cracks was 100 g of m.p. 62°-64°C paraffin, 10 g of m.p. 58°-60°C paraffin and 8 g of vaseline (vaselinum album). However the adding of vaseline prevents cracks and snow-shaped spots but its presence in excessive amount causes a rapid fading of color and decreases the material's sensitivity to radiation. By mixing paraffins of different melting points, the amount of vaseline necessary for preventing the spots and cracks can be decreased. Cracks and snow-shaped spots can still further be eliminated when beeswax or fluid paraffin are used instead of vaseline. In such a case, however, there is marked decrease in sensitivity and a rapid fading of color.
In the paraffin base made in accordance with the writers' prescription snow shaped spots and cracks seldom occur. Furthermore, this material has a high sensitivity to radiations and the color produced by radiations is highly stable.

For these reasons, in the experiments that follow, paraffin + vaseline base is used exclusively. As a base, M.S. Potsaid and G. Irie used "Tissuemat" a commercial product manufactured by Fisher Co., U.S.A. (chemical composition unknown) which is presumably a mixture of paraffin and plastic materials. Compared with the above base, the base made by the authors seems to be superior in the sensitivity to radiation and stability of the changed color.

Exp. 2. Screening of dyes

Chloroform was added as a halogenated compound to the paraffin + vaseline base. And the dyes were screened as follows. Approximately 100 dyes were added singly to the paraffin + vaseline base and exposed to 3,000 r using 80 KVP x-rays (HVL 1.6 mm Al). The results are listed in tables 1, 2 and 3.

While certain dyes did not change color under x-irradiation (Tab. 1), others

| Table 1. Organic compounds in which colors show no change by x-irradiation up to 3000 r |
|---------------------------------|---------------------------------|---------------------------------|
| acridine orange                 | alizarin blue                   | alizarin red S                  |
| aniline gelb                    | auramine O                      | azocarmine G                    |
| azur 1                          | azur-eosine                     | bismarck brown                  |
| boraxcarmine                    | brazilin                        | p-bromophenol hydrazine         |
| canadabalsam                    | carmine                         | carminic acid                   |
| chloral hydrate                 | cholesterin                     | chromogen                       |
| congo red                       | cresylecht violet               | p-diaminobenzene                |
| p-dimethyl-p-phenylenediamine   | p-dimethylamino-benzaldehyde    | 2, 4-dinitroresorcinol          |
| diphenylamine                   | disodium phenylphosphate        | eosine yellowish                |
| erythrosine                     | fuchsine acid                   | glycine                         |
| hematoxyline                    | indigo carmine                  | methenamine                     |
| methyl green                    | methyl orange                   | methylen blue                   |
| monomethyl-p-aminophenol sulfonate | naphthol blue black               | 1-naphthol                      |
| nigrosine                       | nile blue sulfate (delphinblau b) |                                |
| orange G                        | orcein                          | phenolphthalein                 |
| phloridzin                      | phloxine                        | pilocarpin hydrochloride        |
| polychrom-methylene blue        | ponceau 3 R                     | purpurin                        |
| pyronin B                       | phyronin G                      | resorcin                        |
| scarlet red                     | barbital sodium                 | sudan                           |
| thymol                          | tartrazine                      | thionine                        |
| toluidine blue                  | trihydroxymethyl amino-methane  | trypan blue                     |
| water blue                      | urethane                        | dimethylthionine                |
| trimethylthionine               | triaminoazobenzene              | hydrochloride of benzene-m-bis-phenylenediamine |
Table 2. Dyes fade under x-irradiation

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Color Change</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>alizarin</td>
<td>pink — 0</td>
<td>*</td>
</tr>
<tr>
<td>aurantia</td>
<td>pink — 0</td>
<td>*</td>
</tr>
<tr>
<td>brilliant green</td>
<td>green — 0</td>
<td>**</td>
</tr>
<tr>
<td>bromophenol blue</td>
<td>green — 0</td>
<td>*</td>
</tr>
<tr>
<td>dahlia violet</td>
<td>purple — 0</td>
<td>**</td>
</tr>
<tr>
<td>p-diaminobenzene</td>
<td>brown — 0</td>
<td>*</td>
</tr>
<tr>
<td>fuchsine basic</td>
<td>pink — 0</td>
<td>**</td>
</tr>
<tr>
<td>gentian violet</td>
<td>purple — 0</td>
<td>**</td>
</tr>
<tr>
<td>janusgreen</td>
<td>green — 0</td>
<td>*</td>
</tr>
<tr>
<td>neutral red</td>
<td>red — pink</td>
<td>*</td>
</tr>
<tr>
<td>polychrom-methylene blue</td>
<td>pink — 0</td>
<td>***</td>
</tr>
<tr>
<td>sudan black</td>
<td>brown — 0</td>
<td>*</td>
</tr>
</tbody>
</table>

*: color fading is recognized at 3000 r.<br>**: / 1000 r.<br>***: / 500 r.<br>0 denotes colorless

Table 3. Dyes change color under x-irradiation

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Color Change</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylcholine</td>
<td>0 — green</td>
<td>*</td>
</tr>
<tr>
<td>benzidine</td>
<td>0 — green</td>
<td>**</td>
</tr>
<tr>
<td>diazoaminobenzene</td>
<td>yellow — green</td>
<td>**</td>
</tr>
<tr>
<td>dimethyl yellow</td>
<td>yellow — red</td>
<td>***</td>
</tr>
<tr>
<td>diphenylcarbazide</td>
<td>0 — pink</td>
<td>**</td>
</tr>
<tr>
<td>dithizone</td>
<td>green — yellow</td>
<td>***</td>
</tr>
<tr>
<td>methyl red</td>
<td>yellow — red</td>
<td>***</td>
</tr>
<tr>
<td>safranin T</td>
<td>pink — blue</td>
<td>*</td>
</tr>
</tbody>
</table>

*: color change is recognized by 3000 r.<br>**: / 1000 r.<br>***: / 500 r.<br>0 denotes colorless

maintained the same tone under irradiation while its shade became paler (Tab. 2). In others, the main color of the dyes changed under irradiation (Tab. 3).

Of these mixtures, methyl yellow was highly sensitive to the x-rays but relatively unaffected by visible and ultra-violet rays. Methyl yellow was used also in the experiments by M.S. Potsaid and G. Irie. As far as the present experiments are concerned, no other dyes had a higher sensitivity to ionizing radiation and stability to light and temperature than methyl yellow.

Exp. 3. On stabilizers and sensitizers

1. para-hydroxyazobenzene

The addition of 0.1 to 0.2% of para-hydroxyazobenzene to the mixture (the base + chloroform + methyl yellow) made the coloring stable against visible and ultra-violet rays.

Almost no fading of color was seen even when the mixture was left at room temperature for about a week after the irradiation. Furthermore, this addition gave a 5 fold sensitivity as compared against the mixture without para-hydroxyazobenzene. Thus it may be said that para-hydroxyazobenzene functions as a stabilizer and a sensitizer at the same time. Para-hydroxyazobenzene had no sensitizing effect on dyes other than methyl yellow. When carbon tetrachloride or bromoform was used instead of chloroform, no sensitizing or stabilizing effects of para-hydroxyazobenzene were observed.

2. heavy metals

In order to determine whether an addition of heavy metals would increase the sensitivity, BaSO₄ and HgCl₂ were tested. No marked increase in the sensitivity was obtained by the addition of either of these metal compounds.
3. fluorescent materials

Various fluorescent materials were also tested to determine whether the sensitivity would increase, the tested materials are listed in Table 4. The tests revealed that none of these materials increased the sensitivity. From these experiments it may be said that parahydroxyazobenzene is the most suitable material to increase both sensitivity and stability of color.

Exp. 4. On halogenated compounds

Tests were made on various halogenated compounds other than chloroform listed in Table 5. Methyl yellow was used as the dye.

Fluoroform caused an immediate color change even while it was being mixed; this change might be due to the fluorine in fluoroform. Even if this effect can be avoided, its high volatility makes fluoroform unsuitable. Iodoform caused no color change even with the x-irradiation at 10,000 r.

While a mixture with bromoform shows an extremely high sensitivity, but it also has a disadvantage of energy dependency which may be due to the high atomic number of bromine. Another thing is that bromoform is difficult to handle because of its high volatility and poisonous nature. Tri-and tetrachloroethylene showed a low sensitivity. 1,1,1-Trichloro-2, 2-bis-(p-chlorophenyl) ethane has a low volatility but its sensitivity is low. Carbon tetrachloride is highly sensitive when dithizone is used for a dye but shows a low sensitivity when methyl yellow is used. This, combined with its poisonous nature, makes carbon tetrachloride unusable. It was also found that halogenated compounds showed a lowered sensitivity when two or more kinds were used in combination.

From the above experiments it was shown that among various halogenated compounds, chloroform was the most suitable insofar as the present experiments are concerned. An addition of excessive chloroform causes softening of the mixture while too little of it causes a lowered sensitivity. In the present study the following composition (Table 6) was found to be most suitable. This prescription will be referred to as “Mix.-1” herein after.

Exp. 5. On the properties of Mix.-1

Mix.-1 is physically similar to solid paraffin; it is yellow in color, with a light comparatively glossy surface. When Mix.-1 is
irradiated, its color changes from yellow to red in proportion to the radiation dose absorbed (Plate 1). Irradiated Mix.–1 is restored to its original color by melting with heat and washing with water, thus it can be used repeatedly. When left at room temperature the color of Mix.–1 immediately after exposure to irradiation, fades to a certain point but thereafter shown hardly any change for a week. When the irradiated Mix.–1 is placed in a desiccator and the pressure is decreased by means of a vacuum pump, its color fades markedly.

The faded color, however, returns to the original shade when chloroform is added. From these facts it may be assumed that the evaporation of chloroform is one of the causes of the fading of color.

The mixture of paraffin and methyl yellow is yellow and transparent when it is melted. Microscopic observation of a drop of the melted mixture placed on a slide glass, with a coverglass, reveals that yellow crystals of methyl yellow form as the solidification of the mixture proceeds. When vaseline is added to the above mentioned mixture, yellow droplets appear dispersively among the crystallized paraffin with the progress of solidification. A similar examination was also made of the mixture of paraffin, vaseline, chloroform and methyl yellow. The findings were the same as those on the mixture without an addition of chloroform. The writers' Mix.–1 also showed almost the same findings (Plate 2).

Similar examinations on dithizone reveals that paraffin is not separated from dithizone upon solidification.

In brief, Mix.–1 is an uneven material whose chemical and physical characteristics vary microscopically from portion to portion. In the droplets, where reaction may occur exclusively under irradiation, its chemical and physical properties can be quite different from the average of the mixture as a whole. The sensitivity of Mix.–1 is to a great extent independent of the density of methyl yellow. However, the density of dithizone influences the sensitivity markedly.

Such differences in the “density effects” of methyl yellow and dithizone may be presumed as indicated by the microscopic findings. The point indicated above should be considered in future studies of the mechanism of the reaction in Mix.–1.

Fxp. 6. Measurement of absorbed dose

One of the important points of the present study is to determine the absorbed dose through physical and chemical changes in the Mix.–1. For this purpose the following studies were made. Details of the following experiment will be published elsewhere.

1. electric measurement

Plane metal electrodes ca. 40 cm² were placed parallel on both sides of a 2 cm slab of Mix.–1. Then 6 V (D.C.) was applied between the two electrodes and the electric resistance was determined by measuring the current by means of a μμ-ammeter. Irradiation of 10⁵ r caused only a slight change in electric resistance. The measurement of Q value and tan δ by means of capacitance bridge at 50–120 c.p.s. revealed that even irradiation at 10⁶ r showed no influence. These tests
suggest that measurement of the absorbed dose by changes in the electric properties of Mix.-1 is almost impossible.

2. optical measurement of spectral reflection rate

Spectral reflection rate of Mix.-1 of 1 cm thickness, was measured by means of a photoelectric spectrophotometer. As shown in Fig.-1, spectral reflection rate showed different curves according to different absorbed doses, but no simple relationship between them was observable. Hence, this method was ruled out.

3. measurement of acid formed

The acid formed by the irradiation was extracted by deionized water, and measured by a pH-meter. Ten grams of Mix.-1 melted with more than 10 cc of water was shaken well and then was left till water was separated completely. The pH value of the separated water was measured by means of a pH-meter. Then the amount of acid extracted in the water was computed. As shown in Fig. 2, it was shown that a linear relationship existed between the amount of acid formed and the irradiated dose up to 5,000 r.

In this case G-value was about 0.3 which is much smaller than the G-value of liquid chloroform and rather close to the G value of molecular dissociation of paraffin caused by irradiation.

Of the quantitative measurements noted above and those which are now under investigation, this method seems to be the most reliable. In the present studies,
this method was used for measuring the average absorbed dose in non-homogeneous irradiation such as sieve irradiation or radium needling.

A search is underway to find a detector for a mixture of more than two kinds of dyes which exhibit different color responses according to absorbed doses. To date only one detector has been found that satisfied this purpose. It was obtained by mixing the dyes and halogenated compounds that are listed in Table 7 below. Color change of the detector is shown in the appended illustration (Plate 3). This
mixture will be hereafter referred to as Mix.-2. The use of Mix.-2 offers various advantages in that the radiation dose can be determined not by the change in the intensity of color but by the qualitative change in color. If its sensitivity can be heightened, multi-color pictures of x-rays will become available.

**DISCUSSION AND SUMMARY**

As a base material for a solid chemical dosimeter, paraffin is the most satisfactory at present. Water soluble materials such as gelatin or methyl cellulose are not satisfactory as base material.

Plastic materials and fats do not possess suitable physical properties when chloroform is used. Thus, paraffin, which M. S. Potsaid and G. Irie used, is almost fully satisfactory as a base. In order to prevent snow-shaped spots and cracks which often appear after solidification of base, a small amount of vaseline was added in place of beeswax. By using two kinds of paraffin in combination with different melting points, the amount of vaseline required is reduced and color fading of irradiated Mix.-1 can be avoided to a great extent.

Screening tests conducted on dyes showed that as far as we know, methyl yellow showed different colors corresponding to different radiation doses. This mixture was originally green but with a radiation dose of 3,000 r it turned yellow and with an additional radiation dose of 3,000 r it turned red. In brief, this mixture may be regarded as a multi-color chemical dosimeter. If its sensitivity can be increased to some extent, it may even possible to obtain multi-colored x-ray pictures.

As a dye, methyl yellow shows the highest sensitivity and stability. A radiation dose of over 1,000 r is necessary, however, before the change of color becomes noticeable.

In the present study attempts were made to increase the sensitivity of the mixture to radiations by sensitizing agents and parahydroxyazobenzene was found to be the best so far. When parahydroxyazobenzene is added, the change of color is observable with a radiation dose at 200-300 r, which means that the sensitivity of the mixture is 3-5 times greater than that of a mixture in which methyl yellow alone is used. In general, an increase of sensitivity of a system is followed by a decrease in stability. The use of parahydroxyazobenzene, however, heightens the sensitivity without noticeably increasing the susceptibility to influences by visible rays and to fading. This fact means that parahydroxyazobenzene functions as a stabilizer as well as a sensitizer.

A series of tests conducted on halogenated chemicals revealed that chloroform is the most suitable.
In short, the most suitable dosimeter known at present is Mix.-1. This mixture is a yellow solid which changes its color into red when irradiated. This change of color becomes clearly noticeable with radiation doses as low as 200-300 r.

However this sensitivity is not high enough to be used for certain routine clinical work. It is, however, sufficiently usable in determining three dimensional dose distribution. The exact absorbed dose in any portion of the mixture can be obtained by measuring the acid formed in that portion. In a non-homogeneous irradiation, the average absorption dose in a given volume can be obtained by this dosimeter. If its sensitivity can be further increased, it will be possible to widen the scope of its application and it may eventually be used routinely in radiation therapy and in taking colored x-rays pictures.

Its microscopic picture is uneven. Hence, the process of reaction of this mixture may be quite different from that of liquid dosimeters. The writers' studies in the measurement of the exact absorbed dose in the mixture revealed that at present the best method is to extract the acid formed in the mixture and to determine the amount of the formed acid in gram equivalent by measuring the pH value of the extracted solution.

Further research is being conducted using electron spin resonance to clarify the mechanisms of the reaction in the mixture.

CONCLUSION

As a result of the present studies on solid chemical dosimeter the following conclusions were reached:

1. A mixture of 100 g of paraffin at m.p. 62°-64 °C, 10 g of paraffin at m.p. 58°-60 °C and 8 g of vaseline is most suitable as the base.
2. A series of tests on varions dyes reveal that methyl yellow is the best.
3. Chloroform is the most usable halogenated compound.
4. Para hydroxyazobenzene is excellent not only as a sensitized but also as a stabilizer.
5. A mixture of these is named Mix.-1 for convenience' sake. Its color change is detectable at about 200 r.
6. A mixture including two kinds of dyes (methyl yellow and dithizone) showed different colors according to the dose of irradiation. This mixture is named Mix.-2 for convenience' sake.

ACKNOWLEDGMENT

The writers wish to express their thanks for the financial support of Ministry of Education of Japan.
Plate 1.
Photograph of colored cut surface of a block of Mix.-1 exposed to x-rays (right red stripe) and gammarays (left red stripe) from small ports 3 x 3 cm² at upper edge. Color of irradiated parts changes from yellow to red according to the dose absorbed.
x-rays: 200 kVp, HVL: 1.7 mm Cu, FSD: 50 cm, gammarays: 60 Co, FSD: 65 cm.

Plate 2.
Microphotograph of Mix.-1 (ca. x100).
Inhomogeneity of Mix.-1 is shown clearly.

Plate 3.
Photograph of Mix.-2
green part: nonirradiated
yellow part: about 3,000 r x-irradiated
red part: about 6,000 r x-irradiated

REFERENCES