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# A STUDY OF PREVENTION OF SPONTANEOUS LUMINESCENCE OF LUMINOL

[Following is a translation of an article by M. Arai in the Japanese-language journal, Kagaku Keisatsu Kenkyusho Hoko (Reports of Scientific Police Research Center), Vol 15 No 1, 1962, pp 24-26.]

## 1. Introduction

Two methods are conceivable in preventing the spontaneous luminescence of a Luminol reagent. One is to reduce the alkalinity of sodium carbonate by adding some reagents of weak acidity. ~~Indanthrone-4-carboxylic~~ acid and uric acid are used for this purpose. The other method is to add reagents that suppress the decomposition of hydrogen peroxide. In light of the fact that luminous substances such as blood-stains and similar stains accelerate the decomposition of hydrogen peroxide, this method is one of the few that comes to mind first. ~~With such reasoning, we have~~ applied hydroquinone for the purpose of preventing the spontaneous luminescence of the luminol reagent that has a suppressive effect on the decomposition of hydrogen peroxide. The present report deals with the obtained data from the application of hydroquinone.

## 2. Experimental Materials and Methods

### A. Experimental Materials

1. Luminol
2. Sodium carbonate anhydride
3. 30% hydrogen peroxide
4. Indanthrone-4-carboxylic acid

5. Hydroquinone
6. Blood-stained papers

Human blood diluted with a saline solution by the factor of 1, 10, 100, 1,000, 2,000, 4,000, 8,000, 10,000, 20,000, 40,000, 80,000, and 160,000 is stained on the paper and dried for at least one month.

7. Powder used for taking fingerprints (5 kinds)
8. Mist sprayer
9. Metal plates (5 kinds)
10. Common Utensils (10 kinds)
11. Chemicals (20 kinds)

B. Preparation of reagent:

| | | |
|---|---|---|
| luminol | 0.1 g | |
| $Na_2CO_3$ | 5.0 g | ph = 12.0 |
| 30% $H_2O_2$ | 15 cc | |

Add water to make the total volume 100 cc.

C. Experimental method:

1. Experimental determination of the optimal amount of hydroquinone as a preventor of spontaneous luminescence of luminol

Equal amounts of luminol reagent are placed into 10 test tubes and hydroquinone of varying concentrations is added. Luminescence was observed by the naked eye in a dark room after ten of minutes dark-adaptation. Experiments reported in the following all presuppose a ten minutes' dark-adaptation. The concentration levels of hydroquinone used were 0.01%, 0.02%, 0.03%, 0.04%, 0.05% 0.06%, 0.07%, 0.08%, 0.09%, and 0.1%. (Room temperature $30^{\circ}$ - $33^{\circ}$ C)

2. Comparative examination of preventive effects on spontaneous luminescence with hydroquinone and indanthrone-4-carboxylic acid

Two samples of luminol reagents are placed in the test tubes, one with 0.05% of indanthrone-4-carboxylic acid and the other with the optimal amount of hydroquinone, and observed in a dark room for spontaneous luminescence, (room temperature $30^{\circ}$ - $33^{\circ}$ C).

3. Comparative examination of luminescence and intensity on the blood stains of the two spontaneous luminescence preventors (luminol reagents with hydroquinon and indanthrone-4-carboxylic acid, respectively)

The two luminol reagents sprayed on the previously mentioned blood-stained papers of varying dilution, and the duration and intensity of luminescence are measured with the naked eye. (room temperature 30° - 33° C).

4. Comparative examination of characteristics on the blood stain-like luminous substances of the two luminol reagents with hydroquinone and indanthrone-4-carboxylic acid, respectively

Various materials mentioned in the section on experimental materials were divided into two parts, and the two luminol reagents sprayed on them, one reagent on one part. Observations were also made by the naked eye, (room temperature 30° - 33° C).

## 3. Experimental Results

A. On the optimal quantity of added hydroquinone

Addition of hydroquinone to luminol reagent of more than 0.04% did not show any preventive effect on the spontaneous luminescence. Decomposition of hydrogen peroxide water did not show proportional decrease to the added quantity. Therefore, the addition of 0.05% of hydroquinone is considered optimal.

B. Comparison of preventive effects of the two luminol reagents on spontaneous luminescence

Equal quantities of hydroquinone and indanthron-4-carboxylic acid manifest preventive effects on the spontaneous luminescence to a same extent. Luminol reagents placed in the test tubes each with equal amount (0.05%) of hydroquinone and indanthrone-4-carboxylic acid are observed for the duration of their preventive effectiveness. Indanthrone-4-carboxylic acid losses its effect in 40 minutes, whereas hydroquinone manifests its effect upto one hour and thirty minutes.

C. Intensity and duration of luminescence on the blood stains

When the luminol reagents were sprayed on the blood-stained papers, blood stains diluted by the factor of 20,000 were detected by both hydroquinone-added and indanthrone-4-carboxylic acid-added reagents. In terms of the intensity and duration of luminescence, the hydroquinone-added luminol reagent seems equally effective, and almost a little superior to the other one.

D. On the examination of relative characteristics on the blood-stain like luminescent substances (other than blood stains)

1. Fingerprint powder

Golden lead powder showed luminescence similar to the blood stains, but no trace of such luminescence was detected with aluminum powder, black lead powder, black powder and yellow powder.

2. Metal plates

Luminescence similar to the blood stains was observed with copper and brass plates, whereas none was detected with galvanized iron plate, tin(galvanized) iron plate and duralumin.

3. Household items

Luminescence similar to the blood stains was observed with fresh raddish syrup, fresh potatoe syrup, milk and coffee, but none was detected with shoe-cream, grapefruit juice, mineral oils and wood.

4. Chemicals

Luminescence similar to that of the blood stains was observed with sodium carbon anhydride, sodium sulfurous anhydride, ammonium sulfate, copper sulfate, ferrous sulfate, iron(II) sulfate, ferrous chloride, iron(II) chloride, nickel sulfate, cobalt nitrate, potassium permanganate, and red prussiate of potash, whereas none was detectable with potassium chromate, potassium dichromate, barium hydroxide, barium chloride, yellow prussiate of potash, sodium chloride, and potassium chloride.

The blood stain-like luminescence of the above mentioned substances was observable with both hydroquinone-added and indanthrone-4-carboxylic acid added luminol reagents. Little difference was found between the two luminol reagents in terms of the characteristics on the blood

stain-like luminous substances.

## 4. Conclusions

As far as the preventive effectiveness on the spontaneous luminescence is concerned, both hydroquinone and indanthrone-4-carboxylic acid are equally potent, but the former excells the latter two-fold in its duration of preventive effectiveness. Hydroquinone is not inferior in its luminocity on the blood stain and does not show any peculiarity on the blood stain-like luminescent substances; it may well substitute for indanthrone-4-carboxylic acid.

## 5. Postscriptive remarks

Despite some quantitative difference, addition of a preventive agent of spontaneous luminescence into luminol reagent suppresses the luminescent function in the blood stain. Thus, production of luminol reagent without preventor of spontaneous luminescence would assure 100% efficiency, which is highly desirable.

The idea of substituting chemicals of weak alkalinity for sodium carbon anhydride comes very readily. We have examined the matter with various chemicals of weak alkalinity, the results of which are reported below.

The luminocity (spontaneous) decreases as the alkalinity of the chemicals weakens, and sometimes the spontaneous luminescence is not observable. On the other hand, the solubility of luminol decreases in proportion to the decrease of alkalinity. Therefore, luminescence on the blood stains can reasonably be considered to decrease with low alkalinity.

Implications are that prevention of spontaneous luminescence could be accomplished by lowering the alkalinity, while a boost of luminescence would result from increasing the alkalinity.

This, however, is not unexpected. Absence of spontaneous luminescence becomes meaningless if accompanied by weakened luminescence in the blood stains. Ideally, abscence of spontaneous luminescence should be accompanied by increased luminescence on the blood stains. Examining a variety of chemicals, the use of photographic alkaline Nabokusu (Fuji Film) turned out most effective. The preparation is given below;

| | | |
|---|---|---|
| Luminol | 0.1 g | |
| Nabokusu | 5.0 g | ph = 11.2 |
| 30% $H_2O_2$ | 15 cc | |

Add water to make 100 cc.

This reagent shows no sign of spontaneous luminescence, while its luminescence on the blood stains is equivalent to that with sodium carbonate anhydride.

In search for a luminol reagent without spontaneous luminescence but with increased luminescence and longer duration of luminescence on the blood stains, we have tried out the following.

Comparison with sodium carbonate peroxide

$Na_2O_2$ 0.5 g
Add water to the volume 100 cc ph = 13.0

An examination of the luminol reagent with sodium carbonate peroxide indicates reduced spontaneous luminescence and increased luminescence on the blood stains, with longer duration in contrast to the reagent with sodium carbonate anhydride.

However, the reaction of sodium carbonate peroxide is violent and inconvenient to handle due to its moisture absorption, even during the process of weighing. Consequently, a question was posed whether sodium carbonate peroxide could be substituted by sodium hydroxided and hydrogen peroxide. A small amount of dilute sodium hydroxide was added to the luminol reagent with the aforementioned Nabokusu, upon which the luminescence on the blood stains was increased and duration of luminescence lengthened, though spontaneous luminescence was slightly increased, too. Increase of the spontaneous luminescence was very slight compared to the increase of luminescence on blood stains, which encouraged us to proceed with dilute sodium hydroxide and hydrogen peroxide added to the luminol reagent.

Due to easier manageability of hydrogen peroxide water of 3% rather than 30%, preparation of the reagent proceeded as follows.

Luminol 0.1 g
10% NaOH 5 cc ph = 13
3% $H_2O_2$ 5 cc
Add water to make the volume 100 cc.

This reagent shows luminescence on the blood stain stronger than the one with sodium carbonate anhydride, longer duration of luminescence and a reduced degree of spontaneous

luminescence. This reagent could well be used without the addition of a suppressor of spontaneous luminescence.

Since sodium hydroxide is more manageable in the form of a solution, the experiment was carried out, despite the aforementioned preparation, by dissolving 0.1 g of luminol in 50 cc of 1% sodium hydroxide solution and adding 50 cc of 0.3% hydrogen peroxide.

As has been stated, this preparation of the reagent has succeeded in prevention of spontaneous luminescence, increased luminescence of blood stains and a longer duration of luminescence. There remain, however, a few questions that have to be answered, namely the question of characteristics on the blood stain-like luminescent substances and the effect on the determination of blood type of the sprayed blood stains.

The present report summarizes our work up to the present. And we should like to address ourselves to the unanswered questions in a forthcoming paper.

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