

# Effect of Hydrazine on Chemiluminescence Intensity produced during reaction between Luminol and Hexacyanoferrate in alkaline medium

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### Abstract

The Chemiluminescence properties of Luminol and Hexacyanoferrate in alkaline medium were studied in presence of Hydrazine. It was observed that the oxidation of hydrazine by potassium hexacyanoferrate(III) in alkaline luminol solution may be leads to decrease the strong Chemiluminescence signal produced by the reaction between luminol and hexacyanoferrate (III). The decreased Chemiluminescence intensity was proportional to hydrazine concentration in the range of  $5.0 \times 10^{-9} \text{ g-mL}^{-1}$  to  $4.0 \times 10^{-5} \text{ g-mL}^{-1}$ . This can be used to determine hydrazine.

Keywords:Luminol-Hexacyanoferrate Chemiluminescence, Hydrazine

### 1. Introduction

Chemiluminescence (CL) and bioluminescence (BL) are natural phenomena which have attracted the attention of mankind since the evolution of life on the earth. Chemiluminescence, the production of light during a chemical reaction, has proved to be a useful phenomenon in the laboratory and is finding ever increasing applications in analytical chemistry. Current researches on CL are focused in two general directions. One is the discovery of new CL reactions and investigation of their applicability for analysis of real samples and the other direction is the creation of CL detection systems for newly developed separation techniques. Researches on new CL reactions are very important since they open new horizons for the technique. However, sometimes the study of the mechanism of the reaction is bypassed and emphasis is given to the applications only. Nevertheless, a detailed study would help in studying and improving the analytical performance of the procedure.

CL based on the oxidation of luminol (LH<sub>2</sub>) (5-amino-2,3dihydro-1,4-phthalazinedione) is one of the most extensively studied and best known CL system [1-3]. The oxidation is usually carried out in an alkaline medium using an oxidant such as hydrogen peroxide [4], hypochlorite [5], permanganate [6], or hexacyanoferrate (III) [7]. The luminol-hexacyanoferrate system is one of the most efficient CL systems known to date. Luminol-CL in water is mostly applied for analytical purposes, in special forensic medicine (to detect trace amounts of blood); this is why luminol reaction in water has been intensely investigated. Hydrazine is often used as high-energy propellant in space shuttle program, and it is an important precursor in polymer industry, pesticides, and pharmaceuticals [8,9]. However, owing to its intensive mammalian toxicity, the monitoring of hydrazine residues in environment matrices has become a priority field in industrial laboratories. In the present paper, the effect of hydrazine on the intensity of CL produced during reaction between luminol and hexacyanoferrate (III) is reported.

### 2. Experimental details

### 2.1 Materials :

Luminol (from Thomas backer), NaOH, potassium hexacyanoferrate (III), hydrazine (all from E merck, AR/GR grade) used were of spectroscopic grade and were further distilled before use. Triple distilled water was used throughout during the studies.

### 2.2 Solutions preparation :

For the present investigation,  $1.0 \times 10^{-3} \text{ mol-L}^{-1}$ Luminol and  $4.0 \times 10^{-2} \text{ mol-L}^{-1}$  NaOH, were taken. This was the stock solution of Luminol. For the preparation of second solution,  $2.0 \times 10^{-5} \text{ mol-L}^{-1}$  potassium hexacyanoferrate (III) and different amount of hydrazine were taken.

### 2.3 Instruments and Methods :

All the experiments were performed on a chemiluminometer setup connected to a X-Y recorder (Fig.1). Stock solution of luminol (1ml) was taken in reaction cell and potassium hexacyanoferrate (III) solution (1ml) was added through syringe.



## International Journal of Luminescence and its applications Volume 3(II), July, 2013, ISSN 2277 – 6362



### 3. Results and Discussion

The CL signal produced by the reaction between luminol and potassium hexacyanoferrate (III) in alkaline medium were studied in presence of hydrazine. It was observed that hydrazine could greatly decrease the strong CL signal produced by the reaction between luminol and hexacyanoferrate (III) in alkaline medium. The decreased CL intensity was linear with hydrazine concentration in the range of  $5.0 \times 10^{-9} \text{ g-mL}^{-1}$  to  $4.0 \times 10^{-5} \text{ g-mL}^{-1}$ , and the limit of detection was  $2.0 \times 10^{-9} \text{ g-mL}^{-1}$  (36) with a relative standard deviation of  $2.4 \sim 4.1\%$  (n = 5).

The structure of luminol (Eq.1) confers acidic properties, so in presence of a base there results the dianionic species  $L^{2-}$  is formed (Eq.2), which on oxidation with hexacyanoferrate (III) yields the 3-Aminophthalate dianion (III) along with release of reaction energy (Eq.3). This energy is absorbed by species III and which forms the excited state (Eq.4) and then returns to ground state with CL emission (Eq.5). Thus 3-aminophthalate is the luminophor of the luminol CL system, and that the emission maximum of the CL reaction is at 425 nm [10, 11].

The oxidation of hydrazine by potassium hexacyanoferrate(III) in alkaline luminol solution may be leads to decrease the strong CL signal produced by the reaction between luminol and hexacyanoferrate (III). Under the conditions selected as described above a calibration graph showed that relative decrease in CL intensity was proportional to hydrazine concentration in the range of 5.0 x  $10^{-9}$  g-mL<sup>-1</sup> to 4.0 x  $10^{-5}$  g-mL<sup>-1</sup>. This can be used to determine hydrazine. A series of standard solutions of hydrazine were determined under the optimized conditions

to test the linearity of the calibration graph. The results are summarized in **Table-1**.



#### Reaction scheme I

### 4. Conclusions

From the study on luminol- potassium hexacyanoferrate(III) CL behavior involving the effect of hydrazine, the important conclusions drawn are:

- (i) Luminol CL depends largely on hydrazine concentration.
- (ii) The decreased CL intensity was linear with hydrazine concentration in the range of  $5.0 \times 10^{-9}$  g-mL<sup>-1</sup> to  $4.0 \times 10^{-5}$  g-mL<sup>-1</sup>.
- (iii) The limit of detection of hydrazine was  $2.0 \times 10^{-9}$  gmL<sup>-1</sup> (36) with a relative standard deviation of  $2.4 \sim 4.1\%$  (n = 5).
- (iv) Effect of hydrazine on luminol- potassium hexacyanoferrate(III) CL can be applied for determination of hydrazine in different samples.

### 5. Acknowledgement

Author is thankful to CSIR (Counsil of Scientific and Industrial Research) for the financial support (Award No. 9/266(63)/2003 EMR-I) and to Head, School of Studies in Chemistry for providing the necessary facilities for the study.

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| Hydrazine concentration<br>(in ng/mL) | <b>Equation</b> $Y = aC + b$ | Correlation<br>coefficient | <b>RSD</b> (n = 5)% | LOD<br>(in ng/mL) |
|---------------------------------------|------------------------------|----------------------------|---------------------|-------------------|
| 0.005~0.01                            | Y=1750C-7.33                 | 0.9966                     | 4.1                 | 2.0<br>(36)       |
| 0.01~0.1                              | Y=284.4C+12.0                | 0.9987                     | 4.0                 |                   |
| 0.1~1.0                               | Y=88.9C+13.0                 | 0.9994                     | 2.9                 |                   |
| 1.0~10.0                              | Y=31.5C+132.0                | 0.9996                     | 2.6                 |                   |
| 10.0~40.0                             | Y=7.7C+212.5                 | 0.9998                     | 2.4                 |                   |

### Table – 1 : Calibration Graph of Hydrazine