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N-[٤-(دی متیل آمینو) بنزیلیدین] بنزوکساید به‌عنوان یک لومینوفر جدید در سیستم نورتابی شیمیایی پراکسی اگزالات برای اندازه‌گیری ساکاروز

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N-[4-(Dimethyl Amino) Benzylidene] Benzoxide as a New Luminophor in Peroxyoxalate Chemiluminescence System for the Determination of Sucrose

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چکیده

در این کار یک سیستم نورتابی شیمیایی کارآمد، با شدت زیاد و برای اولین بار از مشتقی از نایترون، حاصل از واکنش بیس (۶،۴،۲-تری کلرو فنیل) اگزالات (TCPO) با هیدروژن پراکسید در حضور N- [٤-(دی متیل آمینو) بنزیلیدین] بنزاکسید (نایترون) به عنوان یک لومینوفر جدید و سدیم سالیسیلات به عنوان کاتالیزور گزارش شده است. رابطهٔ میان شدت نورتابی شیمیایی و غلظت TCPO، سدیم سالیسیلات، هیدروژن پراکسید و نایترون بررسی شده است. اثر خاموش‌کنندگی یون‌های Fe^{3+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+} و چند ترکیب مختلف شامل ایمیدازول، L– هیستیدین،L– تیروزین، D– (+)– لاکتوز و D– (+)– ساکاروز، در شرایط بهینه با حداکثر شدت نورتابی که در مرحله اول به دست آمده، روی این سیستم نورتاب شیمیایی مورد بررسی قرار گرفته است. اثر خاموش‌کنندگی یون‌های فلزی و ترکیبات ذکر شده روی نورتابی شیمیایی نایترون بررسی و مقادیر ثابت خاموشی K_Q بر اساس معادله اشترن–ولمر محاسبه شده است. اثر خاموش‌کنندگی یون‌های فلزی و ترکیبات ذکر شده روی نورتابی شیمیایی نایترون به ترتیب زیر کاهش یافت: $Co^{2+} > Fe^{3+} > Cu^{2+} > Mn^{2+} > Ni^{2+} > Cd^{2+}$ و در مورد ترکیبات به ترتیب D – (+)– لاکتوز > ایمیدازول > L- تیروزین >L – هیستیدین > D– (+)– ساکاروز به دست آمد. گستره دینامیکی تمام خاموش کننده ها تعیین گردید. با توجه به گستره دینامیکی و حد تشخیص مناسبتر ساکاروز، این ترکیب به عنوان آنالیت در نظر گرفته شد. گستره دینامیکی، حد تشخیص، تکرارپذیری، تکثیرپذیری به ترتیب مقادیر $۱۰^{-۵} \times ۱/۲۰ - ۱۰^{-۷} \times ۶/۶۷$ ، $۱۰^{-۸} \times ۱/۰۰$ ، ۵/۶۲ ٪ ، ۷/۲۵ ٪ برای n=۳ اندازه گیری به دست آمد. برای تعیین صحت روش درصد بازیابی در گستره ۱۰۴/۳ – ۹۷/۴ ٪ به دست آمد. مزاحمت گونه های مختلف بررسی و مزاحمت یون کبالت و لاکتوز بیشترین مقدار بود. ساکاروز تعیین شده با این روش در نمونه چغندر قند ۱۷ درصد به دست آمد که با نتایج به دست آمده از روش های استاندارد مطابقت خوبی داشت.

واژه‌های کلیدی

نورتابی شیمیایی کارآمد پراکسی اگزالات؛ نایترون؛ اثر خاموش کنندگی؛ ساکاروز.

Abstract

In this work, the first, intense and efficient POCL arising from the reaction of bis (2, 4, 6-trichlrophenyl) oxalate (TCPO) with hydrogen peroxide in the presence of N-[4-(dimethyl amino) benzylidene] benzoxide (Nitrone) as a new luminophor has been reported. The relationships between the chemiluminescence intensity and concentrations of all reagents were investigated. The quenching effect of some cations and compounds such as Fe^{3+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+} ions and imidazole, L-Histidine, L-Tyrosine, D-(+)-Lactose, and D-(+)-Sucrose, on the POCL system were investigated. The K_Q values were calculated from Stern–Volmer equation. It was found that the K_Q values decreases in the order: $Co^{2+} > Fe^{3+} > Cu^{2+} > Mn^{2+} > Ni^{2+} > Cd^{2+}$ and D-(+)-Lactose > Imidazole > L-Tyrosine > L-Histidine > D-(+)-Sucrose. Dynamic range and detection limit of all quencher were determined. Sucrose has the best dynamic range and low detection limit, so sucrose considered as an analyte and then the total sucrose extracted from sugar beet as real sample was measured by this proposed method. Dynamic range, detection limit, mean intra-day and inter-day relative standard deviation (RSD%) were 6.67×10^{-7}- 1.20×10^{-5}, 1.0×10^{-8}, 5.62%, 7.25% (n=3) respectively. For accuracy determination, the percentage recovery was found 97.4%- 104.3%. All interferences were investigated and Co^{2+}, D-(+)-Lactose had most interference. Sucrose percentage of the measured sample was 17 percent. These results are comparable with the results of the standard method to determine the sucrose and is acceptable.

Keywords

Efficient Peroxyoxalate Chemiluminescence; Nitrone; Quenching; Effect Sucrose.

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1. INTRODUCTION

Peroxyoxalate chemiluminescence (POCL) is an effective technique for determination of a large variety of analyte, depending on the roles they play in the CL reaction, such as luminophor [1-4], catalyst [5], quencher [6-8] or oxidant [9-10]. POCL is sensitive and sometimes selective technique for determination propose. The reaction has been suggested to follow a chemically initiated electron exchange luminescence (CIEEL) mechanism via the formation of a high-energy intermediate(s) such as 1, 2-dioxetanedione [11-12]. These mechanisms are well known in detail [13-14].

Sucrose is an organic compound that has very important role in many field of human life such as biological, food and pharmaceutical industry. Therefore, it is important to measure sucrose. Spectrophotometric, chemiluminescence, conductometric biosensor, modified multiwall carbon nanotubes/glassy carbon electrode and any other methods for determining sucrose have been proposed [15-20]. Among these methods, fluorescence and chemiluminescence methods have been reported rarely [21-22].

During the last 50 years, many scientists have paid special attention to nitrones due to their successful applications. Nitrones can be used in the synthesis of various natural and biologically active compounds. This product may be used for the study of biological systems. The certain aspects of nitrone chemistry and its application were investigated [23-24]. Nitrones are prepared by several methods well-documented in the primary literature [25]. Pharmaceutical and biochemical application of nitrone such as: potential implication of the chemical properties and bioactivity of nitrone, radical trapping and inhibition of iron-dependent CNS damage by cyclic nitrone and nitrone-related therapeutics were investigated [26-28].

In this article, the first study on the chemiluminescence new derivative of nitrone was reported. The nitrone derivatives have been synthesized via 1, 3-dipolar cycloaddition reactions [5, 29-31]. The POCL reaction of N-[4-(dimethyl amino) benzylidene] Benz oxide (Nitrone), Fig. 1, as a new luminophor was investigated. The relationships between the chemiluminescence intensity and concentrations of Nitrone, sodium salicylate, hydrogen peroxide and TCPO were investigated. The quenching effect of Fe^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+} ions and D-(+)-Lactose, Imidazole, L-Tyrosine, L-Histidine, D-(+)-Sucrose on the chemiluminescence have also been studied. In addition, due to the best dynamic range for sucrose, total sucrose in sugar beet was determined with this new POCL system. Dynamic range, detection limit, relative standard deviation and all interferences were acquired. The aim of this investigation is to introduce a new nitrone derivative as a new luminophor and accessibility of analytical application of this new POCL system.

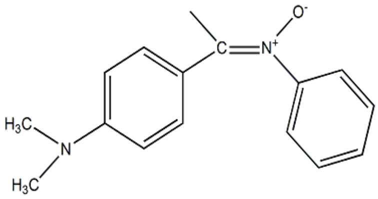

Fig. 1. Chemical structure of naitrone

2. EXPERIMENTAL

2.1. Materials and Apparatus

All chemicals were analytical grade and purchased from Merck and Fluka. TCPO was purchased from Acros ORGANICS and used without further purification. Fluorescence and chemiluminescence spectra were recorded by a Cary Eclipse spectrofluorimeter from Varian Company.

Beets sample was washed and then was grinded. A 20 mg of them is weighted carefully. For sucrose extraction, weighted sample with 100 ml of double distilled water was placed in ultrasonic bath at 50 ° C for 30 min. The sample was filtered before centrifuge. One ml of the sample diluted until 5 ml with ethanol and used as working sucrose solution directly.

2.2. Chemiluminescence Measurements

The chemiluminescence (CL) spectra were recorded after addition of 100.0 µL hydrogen peroxide 3.0 M in ethanol to a 1 cm quartz cell containing 1.0 mL nitrone 1.00×10^{-5} M in ethyl acetate, 1.0 mL TCPO 5.00×10^{-3} M in ethyl acetate and 100 µL sodium salicylate (SS) 1.00×10^{-2}M in ethanol. All measurements were performed at room temperature and in darkness.

2.3. Fluorescence Measurement

The excitation and emission monochromators were set at 290 and 430 nm, respectively. A spectral bandwidth of Em and Ex was 5 nm. The fluorescence spectrum was recorded in a 1 cm quartz cell containing 1.0 mL nitrone 1.00×10^{-5} M in ethyl acetate, 1.0 mL TCPO 5.00×10^{-3}M in ethyl acetate and 100 µL SS 1.00×10^{-2}M in ethanol.

3. RESULT AND DISCUSSION

Peroxyoxalate chemiluminescence (POCL) is well known as one of the most efficient non-biological light producing systems [1, 2, 32-37].

The possible mechanistic pathway for the PO–CL process involves the following steps [38]:

$$\mathrm{TCPO} + \mathrm{H_2O_2} \xrightarrow{K_1} \mathrm{C_2O_4} + 2\mathrm{TCP} \qquad (1)$$

$$\mathrm{C_2O_4} + \mathrm{Naitron} \xrightarrow{k_2} [\mathrm{C_2O_4^- Naitron^+}] \qquad (2)$$

$$[\mathrm{C_2O_4^- Naitron^+}] \xrightarrow{k_3} \mathrm{Naitron^*} + 2\mathrm{CO_2} \qquad (3)$$

$$\mathrm{Naitron^*} \xrightarrow{k_4} \mathrm{Naitron} + h\upsilon \qquad (4)$$

$$\mathrm{Naitron^*} \xrightarrow{k_5} \mathrm{Naitron} + \mathrm{heat} \qquad (5)$$

Where TCPO is 2, 4, 6-trichlorophenol peroxyoxalate. The crucial step in luminescence quenching is assumed the reaction of the quencher Q with the highly energetic intermediate C_2O_4 to give non-chemiluminescent products, in competition with the reaction of luminophor, as follow:

$$C_2O_4 + Q \xrightarrow{k_Q} \text{non chemiluminescentproduct} \qquad (2a)$$

3.1. Optimization of CL conditions

Our preliminary experiments revealed that, the addition of excess amount of hydrogen peroxide to a colorless ethyl acetate solution containing Nitrone, TCPO and SS results a very intense and efficient violet light. In Fig. 2, the CL spectrum for TCPO–H_2O_2 reaction, in the presence of Nitrone is compared with the fluorescence spectrum of the luminophor (Nitrone), obtained under comparable conditions. As is obvious, a good correspondence was obtained for the CL and fluorescence spectral distributions of the luminophor, indicating that the singlet excited state of the fluorescent additive is formed in the reaction and is the emitting species [39, 40]. In addition, relatively high intensity chemiluminescence signal is evident. Fig. 2.

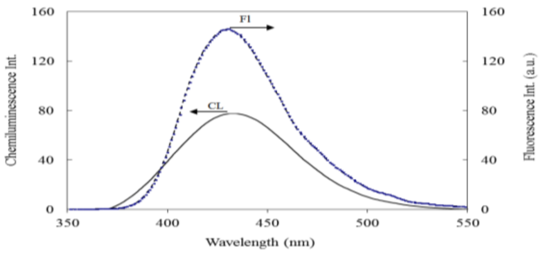

Fig. 2. Fluorescence emission (Fl) and chemiluminescence spectra (CL) of Naitron.

As expected, the initial concentrations of the reactants involved, were found to affect the intensity of the POCL emission [40-42]. Thus, in the next steps, the influence of concentrations of Nitrone, TCPO, H_2O_2 and base catalyst SS, on the POCL system was studied.

3.2. Optimization of Nitrone concentration

The effect of the concentration of Nitrone at constant amounts of TCPO (1.67×10^{-3} M), H_2O_2 (0.10M) and SS (3.33×10^{-3} M), was studied and the results are shown in Fig. 3. In all cases, the peak intensity increases rapidly after mixing and reaches a maximum in few seconds, followed by the decay of light intensity from the maximum. The POCL intensity increased with increasing the concentration of the luminophor until a concentration of 1.33×10^{-6} M was reached. However, further addition of Nitrone resulted in a gradual decrease in the CL intensity.

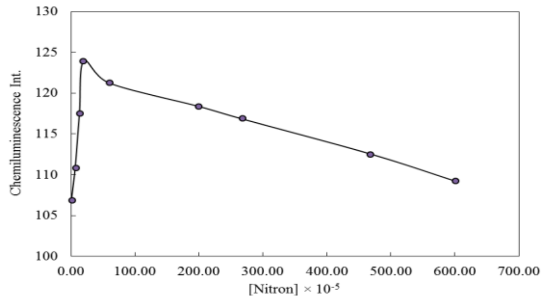

Fig. 3. Effect of varying the concentrations of Naitron on CL intensity in the presence of TCPO (1.67×10^{-3} M)-H_2O_2 (1.02×10^{-1} M)-SS (3.33×10^{-3} M).

3.3. Optimization of TCPO concentration

The influence of the concentration of TCPO on the POCL of Nitrone was studied at constant concentrations of Nitrone (1.33×10^{-6} M), SS (3.33×10^{-3} M) and H_2O_2 (0.10 M) and the results are shown in Fig. 4(a). As it is seen from Fig. 4 the CL intensity increases with increasing concentration of TCPO. A nice linear correlation between the chemiluminescence intensity and the TCPO concentration ($R^2 > 0.99$) was found. The basis for such linear correlation has already been discussed in the literature [11, 43]. Based on these studies, the fourth stage is amplified.

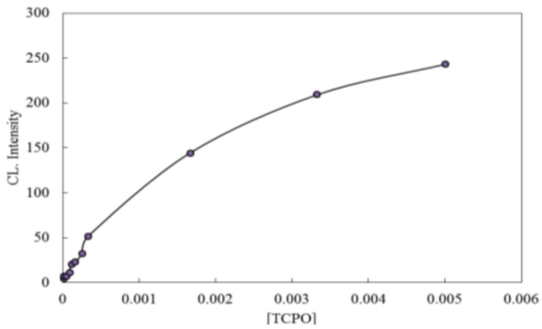

Fig. 4. CL intensity as a function of time for reaction of Naitron (1.33×10^{-6} M), SS (3.33×10^{-3} M) and H_2O_2 (0.10 M), in the presence of varying concentration of TCPO.

3.4. Optimization of sodium salicylate concentration

The POCL intensity of Nitrone, under the optimal constant concentrations of Nitrone and TCPO was found to increase significantly in the presence of sodium salicylate. This behavior is clearly indicative of the catalytic effect of the salt on the POCL system studied [11]. In order to investigate the optimal concentration of sodium salicylate, the CL response of the H_2O_2-TCPO-Nitrone system was measured against the varying concentrations of the base and the resulting plot is shown in Fig. 5. The POCL intensity increased with increasing concentration of sodium salicylate until a concentration of 2.33×10^{-2} M is reached, the observed intensity enhancement being indicative of the catalytic effect of the sodium salicylate. However, further addition of sodium salicylate revealed a gradual decrease in the CL intensity. Higher concentrations of sodium salicylate most probably have quenching effect on chemiluminescence, because higher concentrations of base decompose the reactive intermediate, dioxetane dione, and hence reduces the POCL light [42]. Sodium salicylate is used as a general-base catalyst and imidazole as a nucleophilic and base catalyst. Other reports of POCL indicated that the concentration of imidazole infected the decomposition of the high-energy intermediate and so at low and high concentration of imidazole chemiluminescence intensity are increased and then decreased respectively [44-45].

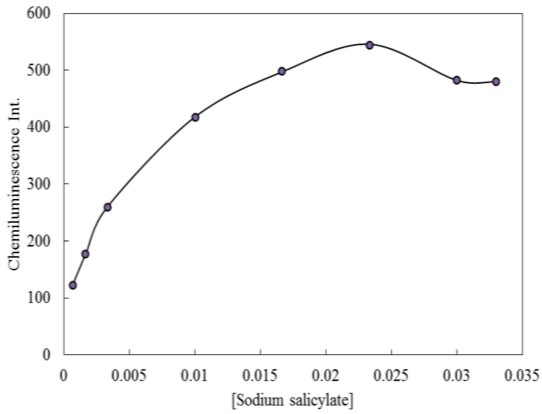

Fig . 5. CL intensity as a function of sodium salicylate concentration for reaction of Naitron (1.33×10^{-6} M), TCPO (5.00×10^{-3} M) and H_2O_2 (0.10 M) in the presence of varying amounts of SS.

3.5. Optimization of hydrogen peroxide

The influence of the concentration of H_2O_2 on the POCL of Nitrone was studied at optimized concentrations of Nitrone (1.33×10^{-6} M), TCPO (5.00×10^{-3} M) and SS (2.33×10^{-2} M) and the results are shown in Fig. 6. As is obvious, the POCL intensity strongly increased with increasing concentration of hydrogen peroxide. It was found that there is a direct linear relationship between the concentration of hydrogen peroxide and POCL intensity of the system, at the concentration ranges studied (i.e., 0.01-0.12 M).

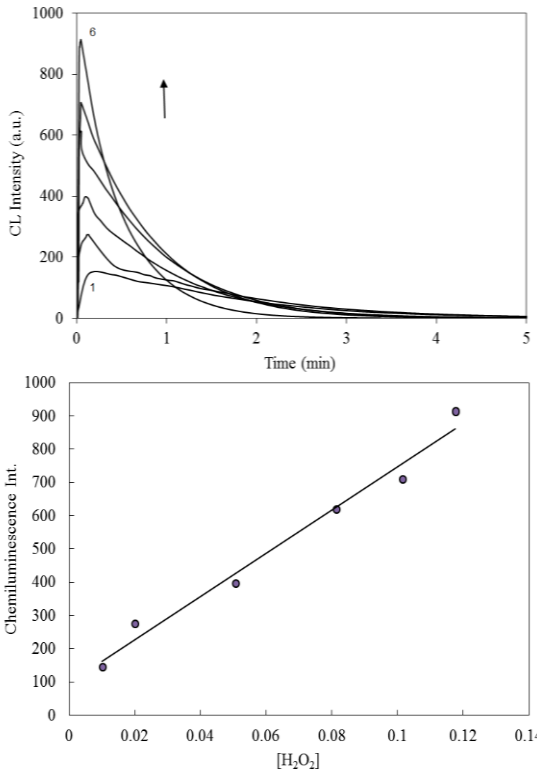

Fig. 6. CL intensity as a function H_2O_2 concentration for reaction of Naitron (1.33×10^{-6} M), TCPO (5.00×10^{-3} M) and SS (2.33×10^{-2}M) in the presence of varying amounts of H_2O_2.

3.6. Quenching effect

Finally, with multistage optimization, the chemiluminescence intensity increases nine times approximately from 100 until 900. Fig. 3 and 6. Then we studied the quenching effect of some cations and compounds on the optimized CL arising from the H_2O_2–TCPO–Nitrone–SS reaction system.

In the present work, in the excess amount of all reagents (H_2O_2–TCPO–Nitrone–SS) relative quencher for comparison purposes, we studied the quenching effect of Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+} and Fe^{3+} ions on the CL arising from the H_2O_2–TCPO–Nitrone–SS reaction system in optimized concentrations. Initial studies clearly revealed that the presence of the metal ions considered can quench the POCL of nitrone significantly. As an example, the resulting CL intensity decay curves for the TCPO–H_2O_2–Nitrone–SS chemiluminescent system in the presence of different concentrations of Cu^{2+} and L–Histidine as an example of metal ions and compounds respectively is shown in Fig. 7a and 7b respectively. The presence of increasing amounts of Cu^{2+} resulted in a significant steady, decrease in the CL intensity–time curves. For the case of other metal ions and compounds, a more or less similar trend were observed.

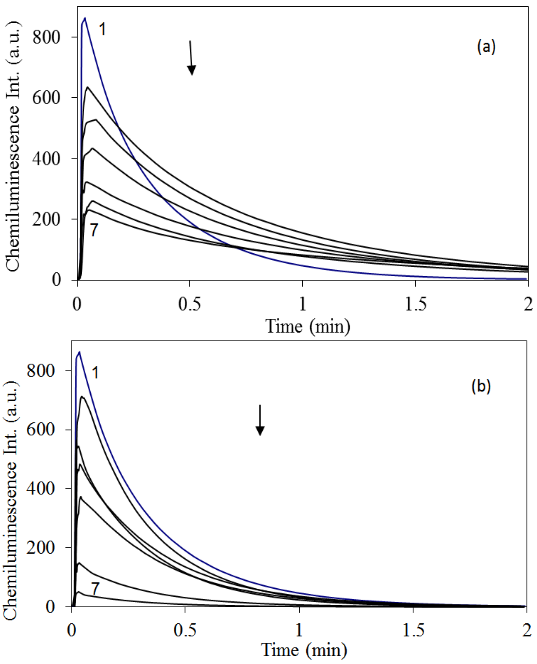

Fig. 7. CL intensity as a function of time for reaction of Naitron (1.33×10^{-6} M), TCPO (5.00×10^{-3} M), SS (2.33×10^{-2}M) and H_2O_2 (0.12M) (a): in the presence of varying concentration of Cu^{+2}: (1) 0.00M, (2) 3.30×10^{-4} M, (3) 5.00×10^{-4} M, (4) 6.00×10^{-4} M, (5) 6.30×10^{-4} M and (6) 8.30×10^{-4} M and (b): in the presence of varying concentration of L–Histidine: (1) 0.00M, (2) 2.50×10^{-4} M, (3) 7.50×10^{-4} M, (4) 1.25×10^{-3} M, (5) 2.0×10^{-3} M, (6) 5.0×10^{-3} M.

For such CL systems, in the presence of a quencher Q, the CL intensity is reduced from I_o to I_Q, the ratio between these quantities being directly proportional to the quencher concentration, as expressed by the Stern–Volmer equation[45-46]:

$$I_o/I_Q = 1 + K_Q[Q]$$

Where K_Q is the Stern–Volmer quenching constant. According to the Stern–Volmer equation, a plot of I_o/I versus [Q] will result in a linear graph with an intercept of 1 and a slope of K_Q. The higher K_Q illustrate that Q have stronger quenching properties. The resulting plots of I_o/I versus the quencher ion concentration for all cations investigated are shown in Fig. 8 (a and b). Also quenching effect of some compounds such as D-(+)–Sucrose, L–Histidine, L-Tyrosine, Imidazole, D-(+) –Lactose were studied. POCL of triazinyl dye as an efficient fluorescence brightener, in the presence of sodium salicylate, imidazol and 4-methylimidazol as base catalysts previously been studied [45]. Imidazole has catalytic effect on POCL system but in this concentration rang imidazole has quenching effect on chemiluminescence intensity. As it is readily seen, the quenching effect of the different metal ions and compounds considered decreases in the order:

$Co^{2+} > Fe^{3+} > Cu^{2+} > Mn^{2+} > Ni^{2+} > Cd^{2+}$

D - (+) –Lactose > Imidazole > L-Tyrosine > L–Histidine > D-(+)–Sucrose

The results are presented in Table 1.

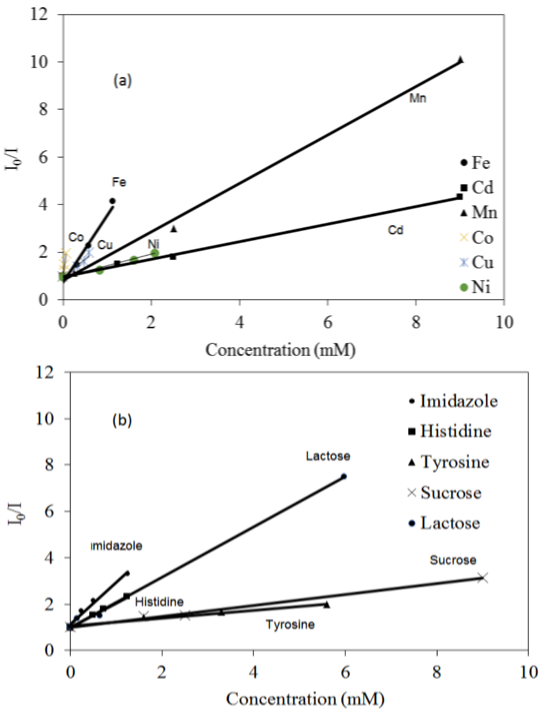

Fig. 8. Stern–Volmer plot of I_o/I versus concentration of different (a) metal ions and (b) compound.

Table 1. Stern Volmer constant, dynamic range and DL of quencher.

Interfere Type	K_Q	Dynamic Range	Detection limit
Co^{2+}	14035.0	1.60×10^{-5} – 1.30×10^{-4}	1.08×10^{-5}
Fe^{3+}	2804.3	3.30×10^{-4} – 1.20×10^{-3}	8.46×10^{-5}
Cu^{2+}	1535.4	3.30×10^{-4} – 6.30×10^{-4}	5.69×10^{-5}
Mn^{2+}	1020.6	2.50×10^{-4} – 9.00×10^{-3}	1.39×10^{-4}
Ni^{2+}	474.2	8.30×10^{-4} – 3.00×10^{-3}	1.98×10^{-4}
Cd^{2+}	369.7	7.50×10^{-4} – 9.00×10^{-3}	6.19×10^{-4}
D-(+) –Lactose	10828.0	1.60×10^{-5} – 6.00×10^{-4}	1.16×10^{-5}
Imidazole	1788.5	2.50×10^{-4} – 2.50×10^{-3}	2.19×10^{-4}
L-Tyrosine	1705.0	3.30×10^{-5} – 5.60×10^{-4}	1.18×10^{-5}
L–Histidine	1046.8	2.50×10^{-4} – 2.00×10^{-3}	1.50×10^{-4}
D-(+)–Sucrose	235.0	6.67×10^{-7} – 1.20×10^{-5}	1.0×10^{-8}

Table 2. Effect of other type on chemiluminescence system in the determination of 1.0×10^{-7} M sucrose.

Interfere Type	$I-I_0$	$I_{100}-I_0$	$\frac{I-I_0}{I_0}\times 100$	$\frac{I_{100}-I_0}{I_0}\times 100$
Ni^{2+}	-106.13	-156.77	-16.44	-24.29
Co^{2+}	-232.90	-398.43	-36.09	-61.74
Cu^{2+}	-149.87	-262.78	-23.22	-40.72
Fe^{3+}	-225.97	-337.87	-35.01	-52.35
Cd^{2+}	-233.23	-230.80	-36.14	-35.76
Mn^{2+}	-219.40	-109.12	-33.99	-16.91
Imidazole	-385.12	-231.11	-59.67	-35.81
D-(+) –Lactose	-457.04	-347.74	-70.82	-53.88
L–Histidine	-274.52	-165.63	-42.54	-25.66
L-Tyrosine	-246.77	59.46	-38.46	9.21

Table 3. Recovery, measured concentration and precision for the determination of sucrose.

Amount Added (M) × 10^{-6}	Amount found (M) × 10^{-6}	Amount Recovered (M) × 10^{-6}	Recovery (%)	Intra-day precision (RSD %)	Inter-day precision (RSD %)
0.5	5.46	0.46	94.02 ± 2.27	5.32	7.35
1.2	6.18	1.18	98.33 ± 3.23	5.73	6.82
3.8	8.97	3.97	104.47 ± 1.51	5.83	7.59

3.7. Sucrose determination

Finally, because large dynamic range and low detection limit of sucrose, ability of this proposed POCL system for determination of sucrose investigated and the total sucrose extracted from sugar beet in real sample was determined. Linear dynamic range, detection limit and relative standard deviation were 6.67×10^{-7}- 1.20×10^{-5}, 1.0×10^{-8}, 5.6% (n=3) respectively. All interferences were investigated and Co^{2+}, D-(+)-Lactose had most interference in the determination of sucrose. All results are presented in Table 2 and 3. For prediction, accuracy of this technique recovery was acquired (97.4%-104.3%).

4. CONCLUSION

In this work, we report for the first time POCL from Nitrone as new intense and very efficient luminophor and found that Nitrone emits a violet-blue light (λ_{max}= 430nm) when it is sensitized in a peroxyoxalate (PO-CL) system and can be used as a strong luminophor. Then, we demonstrated that bivalent metal ions and some compounds have a quenching effect on this new POCL system. There are good correspondence between K_Q as Stern–Volmer quenching constant and interfering of quencher as we report in Table1 and 2. D-(+)-Lactose and Co^{2+} had most interference and K_Q in the determination of Sucrose. This chemiluminescence intensity of nitrone and its interesting application for trace amounts determination of total sucrose are reported. Despite the relatively poor selectivity, this method have good accuracy, simplicity, sensitivity, rapidity and recovery. For accuracy test of this POLC system the recovery 98.7% has been accrued for 1.0×10^{-7} M sucrose (n=4). Therefore, this new method has satisfactory result. This report is the first indirect POCL determination of sucrose and did not need pretreatment or derivatization for of sucrose. Sucrose percentage of the measured sample was 17 percent. These results are comparable with the results of the standard method to determine the sucrose and is acceptable. So, this method may be compares favorably, with previous reported methods [47]. In addition, this new POCL system may be used for determination of hydrogen peroxide Fig. 6.

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