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On line Bromimetric Determination of Sulphonamides Using Flow Injection With Chemiluminescence Detection

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ABSTRACT

Organic compounds that can be brominated by bromine are determined by injection them in acidic solution into bromate-bromide eluent. Unconsumed bromine was monitored using [Br_2-H_2O_2-Luminol] chemiluminesence system. The optimum parameters were studied and were found to be the following: KBr 0.2 M, $KBrO_3$ 0.1M, CH_3COOH 1M, H_2O_2 0.01M, luminol 5×10^{-4} M, flow rate 3.5 ml min^{-1}, and 100 µl sample with frequently of 90h^{-1}, gave working ranges of 10-70 µg ml^{-1}, with precision less than 2%. Detection limits of down to 10 ng per 100 µl sample were obtained. Application to a methoprim tablet was described.

Keywords: Chemiluminesece Detection; Flow Injection; Sulphonamides Determination; Luminol.

Introduction

The analytical utility of chemiluminescence of Luminol has been the subject of extensive study. Ruzicka and Christian [1] used Luminol-CL flow system for determination of organic compound.

Sulphonamides are considerable as the sulphadrugs, although they have supplanted to a wide extent by the antibiotics[2]. It named under a chemotherapic compounds [3], the sense of treatment of diseases, due to bacterial invasion, by chemical compounds, which destroy the micro organisms without affecting the tissues.

Bratton-Marshall method [4] was the most widely used for spectrometric determination of sulphonamide in clinical and research work as the free aryl primary amines is converted to a diazonium salt, the detection limit is 0.5 mg/L in plasma, 1.3 mg/L in urine.

The latter method adapted for FIA by Koupparis et al [5]. Flow injection chemiluminesence system used for determination of sulphonamide as an enhancement for (H_2O_2.Luminol)

chemiluminesences[6]. A simple titrimetric methods depending on the reaction with bromine water[7], and with N-bromophthalamide[8] has been used for determination of sulfadrugs. In both methods the sulphonamides present in the drugs are determined via bromination as an indirect and direct visual titration methods respectively.

On line bromometric methods for determination of Asprin[9] and Phenol [10] by voltammetry and spectrophotometry respectively are known.

In Situ generation of bromine [11], from bromate-bromide-acid using flow injection system, enhances the chemiluminescence of luminol- H2O2 reaction system.

In the present work an on line bromometric determination of sulphonamides by FIA – CL method using (Br_2 – H_2O_2 – Luminol) system depending on that the chemiluminesence intensity which is directly proportional to the concentration of the sulphonamide is dramatically decreased as this due to the consumption of bromine which is generated from the bromate – bromide acid decomposition of hydrogen peroxide, which is necessary for luminol chemiluminscence.

Experimental

Apparatus:

A multi channel prestaltic pump, (Waston – Morfon); a sixway injection valve (7 / 25 – Rheeodyne) flow system chemiluminesence detector type (LKB) 2238 Uvicord SII system chemiluminesence (Kipp & Zone), x – t recorder BD4.

Reagents

The following solutions were prepared:

Sodium carbonate ($Na_2CO_3.10H_2O$) 1M dissolving 28.617 g/L.

Luminol solution 10^{-3}M, dissolving 0.17717 g/L.

Hydrogen peroxide (H_2O_2) 0.1M, dilute 10.3 ml of 35% H_2O_2 in liter.

Potassium bromide, 0.25 M, Potassium bromade 0.25M,

Acetic acid 6M of 99.5% with sp.gr = 1.05,

Sulphonamide 1000ppm, 1g in liter.

General procedure

The schematic diagram in Fig.(1) shows the system used in which 100 µl of acidified sample, with CH_3COOH to final concentration of (1M) is injected through sample loop into a stream of BrO_3^- and Br^- ions to delay coil (100cm), in which Br_2 generated. Later it is reduced by reaction with sulphonamide sample used for deccomposition of H_2O_2, which is necessary for luminol chemiluminesence.

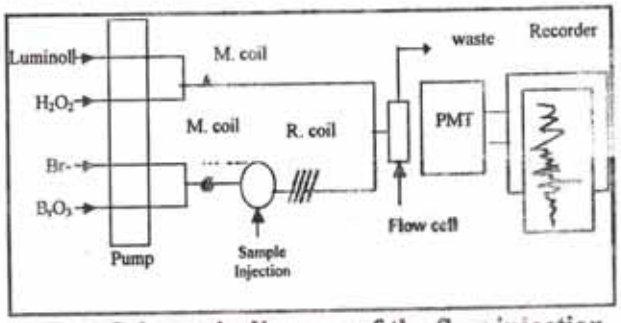


Fig.1 Schematic diagram of the flow injection with Chemiluminesence system used for the determination of sulphonamide.

Optimizations:

1- Physical optimization

a- Effect of flowrate: Effect of flowrates were studied by operating the flow injection Chemiluminesence-manifold is shown in Fig(1). The CL-intensity increases as flow rate increase. 3.5 ml/min was selected as optimum flow rate for obtaining clear response and maximum time required for signal measurement.

b- Effect of delay-reaction coil: Different lengths of delay coil were studied (50-200cm) the results obtained indicated that 100 cm is the best length upon the high CL-intensity, peak profile and time required.

c- Effect of volume sample: Different sample volumes (20-200µl) were injected after adjustment the acidity to a final concentration of 1M with CH_3COOH. 100 µl sample volume loop were selected for the same reason in b.

2-Chemical optimization

a- Effect of Br^- concentration: By fixing all physical parameters different concentrations of Br^- solution were used with 1×10^{-3} M H_2O_2 and 1.0M $KBrO_3$ solutions. By injection 100 µl of sample in different acetic acid concentration (0.25, 0.5, 1.0M). It was found that 2.0×10^{-1} M KBr concentration is suitable concentration to give a maximum chemiluminesence intensity as peak height (mV), as shown in Fig(2).

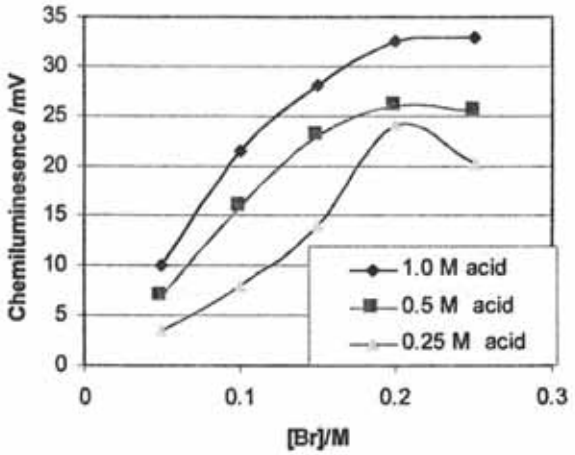


Fig.2 Effect of bromide concentration on chemiluminesence intensity. 1×10-4M luminol, 1×10-3H2O2 and 1.0M KBrO3

b- Effect of BrO_3^- concentration: As before in (a) all parameters were fixed with constant concentration of KBr solution 2.0×10^{-1} M. By using different concentrations of $KBrO_3$ solution, The optimum concentration for maximum chemiluminesence intensity as a peak height (mV) was 1.0×10^{-1} M $KBrO_3$ solution as shown in Fig.(3)

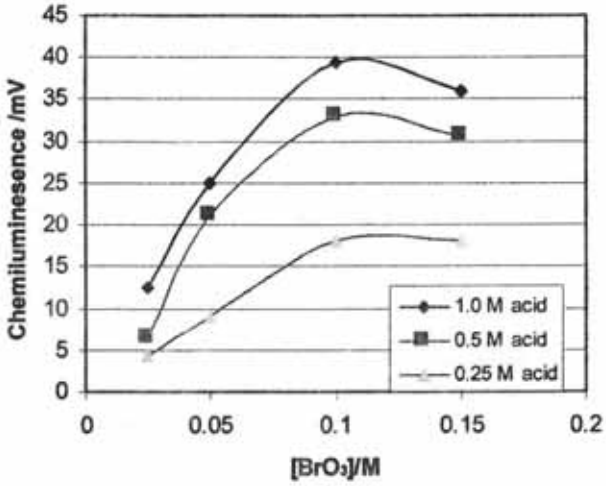


Fig.3 Effect of bromade concentration on chemiluminesence intensity. 1×10^{-4}M luminol, $1\times10^{-3}H_2O_2$ and 2×10^{-2}M KBr.

c- Effect of hydrogen peroxide concentration: By preparing different hydrogen peroxide solutions, and by fixing all parameters as in (b), with 1.0×10^{-1} M $KBrO_3$ solution, Fig.(4) shows the maximum chemiluminesence intensity as a peak height (mV), with 1.0×10^{-2}M hydrogen peroxide concentration.

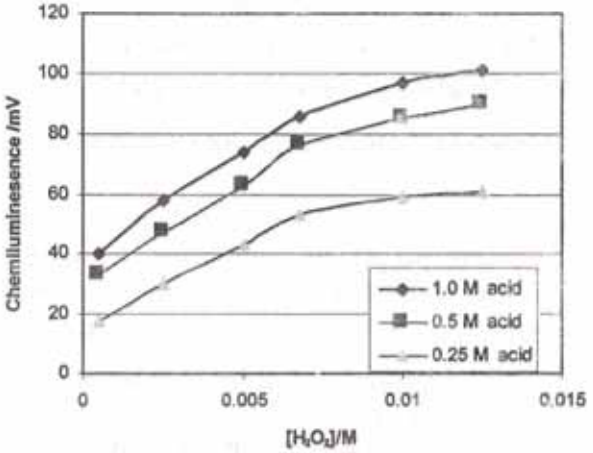


Fig.4 Effect of hydrogen peroxide concentration on the chemiluminesence intensity, optimum concentration 2×10^{-2}M KBr, 1.0×10^{-2} M $KBrO_3$.

d- Effect of luminol concentration: By appropriate dilution of a stock solution of luminol, and fixing all parameters as in (c) with 1.0×10^{-3} M hydrogen peroxide concentration and 1.0 M acetic acid concentration the maximum chemiluminesence intensity was obtained with 5×10^{-4}M luminol concentration as shown in Fig.(5),

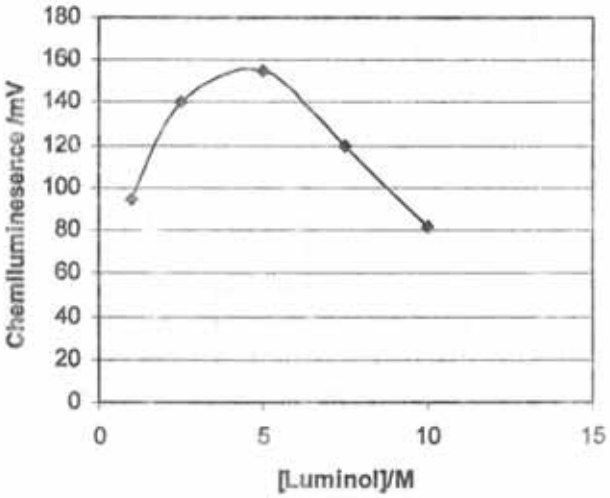


Fig.5 Effect of luminol concentration on the chemiluminesence intensity, optimum concentration 2×10^{-2}M KBr, 1.0×10^{-2} M $KBrO_3$, and 1.0×10^{-3}M H_2O_2.

Calibration Graph

Various concentrations of (1,10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 ppm) of Sulphonamide were prepared using the parameters established above. Each measurement repeated three times. The CL-intensity as a peak height (mV) was plotted against the concentration of sulphonamide, a straight line graph Fig.(6) from 10-70 ppm sulphonamide was obtained. Regression analysis gave the following equation:

$Y=b+ax$

$Y=CL_{emission\ (mv)}$,b=Intercept, a=slope, x=concentration µg/ml

$CL_{emission\ (mv)}$ = 138.7835–1.0665 conc. µg/ml

with correlation coefficient of 0.998. The relative standard deviation (RSD%) is less than 2%.

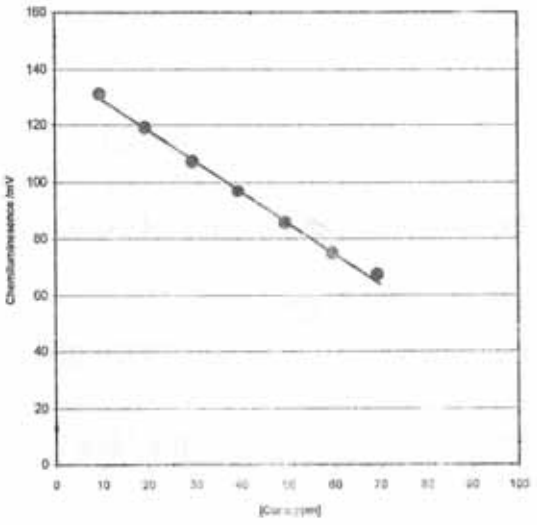


Fig.6 Linear calibration graph for the determination of sulphonamides using flow injection with chemiluminesence detection.

Detection Limit

It is possible to observe that 0.1 ppm sulphonamide is the least concentration that affect (decrease) the intensity of CL.

Applications

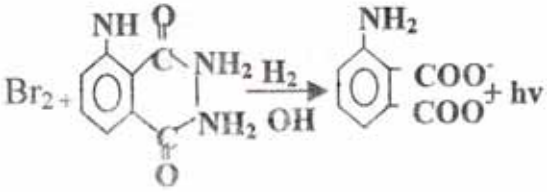
Methoprime tablet contain 400 mg, few tablet were cracked, sieved and weight, a known amount of one tablet then dissolved in 5 ml of 0.5 M acetic acid, then filtered and diluted to 100 ml by distilled water. By appropriate dilution can be reach the determination limit with % recovery = %96.8

Conclusion

The proposed luminol chemiluminesence method for determination of sulphonamide has been applied successfully by FIA-CL method using (luminol-H_2O_2-Br_2) system.

The intensity is decreased by increasing sulphonamide concentration. The proposed mechanism of the reaction related to the method illustrated as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$



If the concentration of Br_2 decreased by its reaction with sulphonamide the CL-intensity decrease simultaneously.

This work if compared with FIA method[7] it is provide high linear range as showing in Fig.6. The selectivity are not less than obtained by Bratton-Marshal method[5].

The method can be used for pharmaceutical analysis.

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بەشی کیمیا/ کۆلیژی پەروەردە

زانکۆی سەلاحەدین- هەولێر - هەرێمی کوردستانی عێراق

پوختە

زۆر لە مادده ئورگانیکەکان بە تایبەتی ئەوانەی لەگەڵ بروم کاریگەری کیمیاوی ئەکەن تقدیر ئەکرێن بە هۆی لێدانی گیراوەی ترشیان بۆ تێکەڵەیەکی بروامات-بروامید.

بەمە ئەتوانین کە بریسکەی کیمیاوی ببینین. ئەمەش بەهۆی ئەو بڕە بروامەی کە دەمێنێتەوە پاش کارلێک کردنی لەگەڵ مادده ئۆرگانیکیەکاندا بە بەکار هێنانی سیستەمی (Br_2-H_2O_2-Luminol).

توانرا لێکۆلینەوەیەکی نموونەیی بکرێت بۆ ئەم کارلێک کردنە لەو سیستەمەدا وە دەرچوو بەم شێوەیەی خوارەوە:

مولاری KBr ، 0.1مولاری KBrO3 ، 1.0 مولاری CH3COOH ، 0.01 مولاری H2O2 ، 5 X 10- 4 مولاری گیراوەی لومینۆل. وە بە خێرایی ٣,٥ ملی لتر بۆ هەر خولەکێک بە بەکارهێنانی ١٠٠ مایکرۆ لیتر لە نمونەکە بە خێرایی 90 نمونە لە کات ژمێرێکدا.

تواندرا لە ڕێژەی 70-10 مایکروگرام بۆ هەر ملی لتر کاربکرێت بە ووردی کەمتر لە 2%.

بینرا کە ١٠ نانۆگرام کەمترین نموونەیە کە بتوانرێت بخەملێنرێت بکرێت لە کاتی حقن کردنی 100 مایکرۆلتر.

توانرا ئەم ڕێگایە جێ بەجێ بکرێت بەسەر سامپلەکانی دەرمانسازی لە تابلیتەکانی میثی پرین.

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قسم الكيمياء / كلية التربية

جامعة صلاح الدين- أربيل- أقليم كردستان - العراق

الخلاصة

يتم تقدير اغلب المركبات العضوية والتي يمكنها التفاعل مع البروم، وذلك بحقن محاليلها المحمضة في تيار مكون من مزيج من محلولي البرومات- البروميد. يمكن الحصول على البريق الكيميائي، اعتمادا على البروم الغير المستهلك نتيجة تفاعلها مع المركبات العضوية، باستخدام منظومة ($Br_2 - H_2O_2 - Luminol$).

درست الظروف المثلى للتفاعل وقد كانت بالشكل التالي: 0.2 مولاري KBr، 0.1 مولاري $KCrO_3$، 1.0مولاري CH_3COOH، 0.01مولاري H_2O_2، $5 X 10^{-4}$ مولاري لمحلول اللومينول و عند سرعة جريان 3.5 ملي لتر لكل دقيقة و بحقن حجم 100 مايكرولتر للنموذج وبسرعة نمذجة تساوي 90 نموذج في الساعة. كانت مدى الخطية يتراوح بين 70-10 مايكرو غرام لكل ملي لتر و بدقة اقل من 2%.

وقد وجدت ان 10 نانوغرام هي اقل حد للكشف عند حقن 100 مايكرولتر. تم تطبيق هذه الطريقة على نماذج صيدلانية من حبوب المثبرين.

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