QUENCHING OF CERENKOV RADIATION FROM NATURALLY OCCURRING ^{40}K BY DYES AS PHOTOMETRIC TECHNIQUE

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ABSTRACT

The beta emitter ^{40}K isotope contained in KCl solutions, produces photons known as Cerenkov radiation measurable by liquid scintillation spectrometry. A set of dyestuffs and metal ion complexes showed quenching effects against Cerenkov light.

Studied systems follow the Stern-Volmer equation. Counting ratios $\left(R_0/R\right)-1$ vs. quencher concentration [Q], are linear, yielding $K_{S\text{-}V}$ constants. High $K_{S\text{-}V}$ values indicate highly quenched systems. Congo red and Methylene blue have K_{S-V} values 20.0×10^{4} M^{-1} and 2.27×10^{4} M^{-1} respectively. Crystal violet does not act as quenching agent in the range up to 0.1mM, and has a lowest K_{S-V} value, about 10^{-4} M^{-1}. There are linear correlations between visible absorbances at λ_{max} and counting ratios $\left(R_0/R\right)-1$.
Neither inorganic colorless salts as lead nitrate or zinc nitrate, nor pure solvents as acetonitrile, acetone, methanol and ethyl acetate showed quenching properties. As a result, a procedure suitable for dyestuff determinations based on quenching of Cerenkov radiation has been accomplished.

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INTRODUCTION

High energy charged particles may enter into materials such as glass, plastic, or water, producing a bluish glow such as in a swimming pool nuclear reactor where energetic particles are emitted. Electrons traveling through water, move faster than the phase velocity of the light in that medium. Apollo astronauts observed flashes of light with their eyes shut attributed to Cerenkov emission caused by cosmic rays entering into their eyes,(1). The emitted light is known as Cerenkov radiation. In a wavelength interval $\Delta\lambda$ the number of photons emitted as Cerenkov light is proportional to $\frac{\left[1-\left(c^2/n^2v^2\right)\right]}{\lambda^2}$ where c is the light velocity, n is the refractive index of the medium and v the velocity of the particle (2),(3). Emitted photons have a continuous spectrum and the condition to produce Cerenkov radiation is giving by:

$$\beta n = 1 \qquad [1]$$

where $\beta = \frac{v}{c}$. If relativistic electrons are involved, β can be written in terms of electron energy E:

$$\beta = \left[1-\left(\frac{1}{\frac{E}{511}+1}\right)^2\right]^{\frac{1}{2}} \qquad [2]$$

For water n =1.332, then β should exceed 0.7508 to produce Cerenkov radiation by electrons. From equation [2], E = 263 KeV , a result for the lower energy threshold of Cerenkov radiation. Cerenkov light is emitted as a cone with angle θ respect to the electron movement direction

$$\cos\theta = \frac{1}{\beta n} \qquad [3]$$

Electrons with the threshold energy value will form a narrow cone. Therefore, there is a maximum angle of emission of 41.3° in water (4).

The content of ^{40}K radioisotope in natural potassium is 0.0117% and decays with a half life of 1.277x10^9 years. Their decay modes include a 89.28% by β emission to the ground state of ^{40}Ca and 10.72 % by electron capture toward an excited state of ^{40}Ar which is followed by emission of gamma rays of 1.460 MeV, (5),(6).

Pulse height shifts due to ^{32}P observed by liquid scintillation spectrometry were related to absorbance of dyes,(7). Works faced with counting efficiency improvement involving dissolved organic compounds, solvents and color quenching have been made,(8),(9),(10). Quenching of Cerenkov radiation by colored substances concerning correlations between concentration and quenching effects including isotope free measurements using external standard were also published,(11),(12),(13). In a study dealing with meta-materials, Cerenkov light has been applied,(14).

Although quenching phenomenon theory has been applied to photochemical reactions where fluorescence are involved, the basic principles are useful as frame,(15),(16),(17). Fluorescence emission processes have been described in terms of Stern-Volmer equation:

$$\frac{\varphi_f^0}{\varphi_f} = 1 + K_{S-V}[Q] \qquad [4]$$

in which φ_f^0/φ_f is a ratio of fluorescence quantum yields, in absence and in presence of a quenching agent . K_{S-V} is the Stern-Volmer constant that involves a bimolecular quenching rate constant k and τ_0 the excited state life time in the absence of quencher. $[Q]$ is the molar concentration of quencher molecules. Instead of the quantum yield ratio; photon detector response ratios R_0/R are currently used. From linear relationships between (R_0/R)-1 and $[Q]$, K_{S-V} constants can be evaluated. The aim of this study is to report a series of data concerning Cerenkov light quenching effects exerted by different compounds playing the role of analyte in aqueous medium, using ^{40}K. natural radioisotope as β emitter. A photometric technique to quantify organic dye molecules and metal ion complexes based upon quenched light are presented. In the frame of Stern-Volmer equation, detection limits, linear ranges and limitations are also evaluated.

RESULTS AND DISCUSSION

The Liquid Scintillation system enables Cerenkov light detection from ^{40}K contained in potassium chloride salt dissolved in water. Figure 1 shows that counting rate is proportional to potassium chloride concentrations. Progressive additions of Methyl orange stock solution, cause a drop in counting rate or quenching along the tested range. However, each dye produces a different counting drop as a feature showing different slope values.

Counting rate R_0 due to KCl solutions in absence of quencher or dye and counting rate R measured after dye solution additions. From both readings ratio values as $(R_0/R) - 1$ versus concentration $[Q]$, yielded straight lines from which $K_{S\text{-}V}$ constants were calculated. All studied systems were found to be linear over an established concentration range. Some Stern-Volmer plots are represented in figure 2 where different slopes may be seen.

Congo red has a $K_{S\text{-}V}$ value of 20.0x10^4 M^{-1} a high value compared to the others, therefore it has a good quenching ability. The low $K_{S\text{-}V}$ value for Brilliant green, shows its low quenching effectiveness. On the other hand, Crystal violet has a lowest $K_{S\text{-}V}$, around 10^{-4}; such a striking difference points out that there is no quenching effect within the studied concentration range. A set of Stern-Volmer constants $K_{S\text{-}V}$ are shown in table 1, together with characteristic visible light absorption wavelengths and molar absorptivities.
On the basis of the analysis of visible absorption spectra, there is good correlation between absorbance values and

Cerenkov light quenching ratios. Figure 3 illustrates some relationships between visible light absorbances at λ_{max} and $\left({}^{R_0}/_{R}\right) - 1$ values. These straight lines indicate fairly that Cerenkov photometry might be an amenable analytical technique. However, a question would be how to analyze mixed dyes.

Although there is no correlation between visible spectroscopy parameter ε , the molar absorptivity arising from absorbances and K_{S-V} , Stern-Volmer constants could be parameters alike ε.

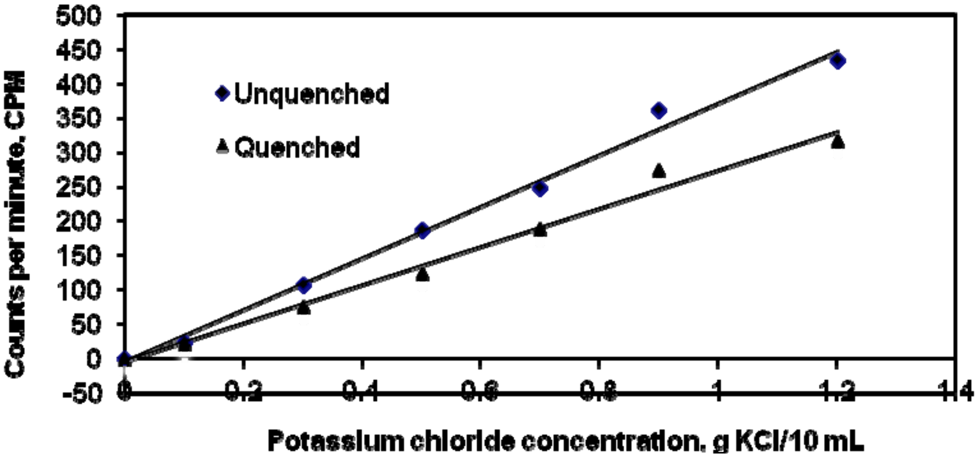

Fig.1. *Detected differences between unquenched and quenched potassium chloride solutions by dissolved Methyl Orange.*

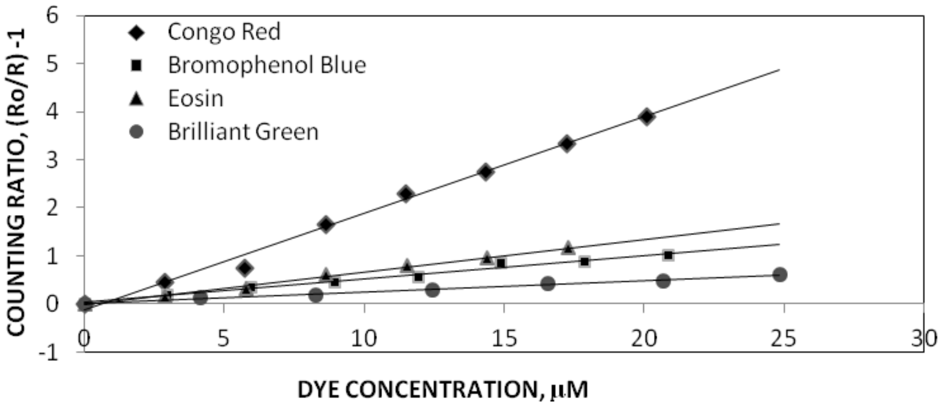

Fig.2. *Stern-Volmer quenching plots of Cerenkov radiation upon addition of different dyes.*

Additions of pure solvents such as acetone, acetonitrile, methanol and ethyl acetate to KCl solutions separately, did not show quenching effects. Nevertheless, this fact could be an advantage because solvents other than water may be used in this kind of measurements. Dissolved lead and zinc nitrates are also unable to produce quenching . Neither high concentrations, nor long data acquisition times gave detectable quenching.

According to data, a high dye concentration does not cause further decrease of counting rate. Moreover, low counting rates due to high dye concentration would be an additional source of uncertainty.

Detection limits considered as the lowest concentrations which can be detected, are roughly 2 or 3 p.p.m. A high detection limit belongs to the Crystal violet. The linear range column indicates the upper limit of concentration range with a correlation coefficients near 0.9990. Table 2 summarizes these parameters. This quenching technique not only has low detection limit, but also has good calibration linear relationships. Prepared standard solutions measured as "unknowns" gave relative standard deviations (RSD) around 3-5%. However, it depends on the kind of dye measured and RSD values were all below 10%, but the Crystal violet. Despite of micromolar concentrations, these ones were also expressed in mg/L or p.p.m.

***Table 1**. Values of Stern-Volmer constants and visible spectra parameters of dyes and inorganic ions.*

Compound/Dye	$K_{S\text{-}V}$, M^{-1}	λ_{max} , nm	ε , cm^{-1} M^{-1}
Malachite Green	$7.44x10^4$	618	$7.04x10^4$
Murexide	$2.07x10^4$	525	$6.64x10^3$
Brilliant Green	$2.38x10^4$	625	$6.30x10^4$
Methylene Blue	$2.27x10^4$	665	$8.52x10^4$
Methyl Orange	$16.1x10^4$	505	$1.64x10^4$
Congo Red	$20.0x10^4$	497	$5.83x10^4$
Methyl Red	$15.2x10^4$	437	$1.60x10^4$
Neutral Red	$9.91x10^4$	540	$2.96x10^4$
Eosin Y	$6.84x10^4$	516	$8.23x10^4$
Bromophenol Blue	$4.81x10^4$	589	$3.18x10^4$
Crystal Violet	$1.85x10^{-4}$	589	$7.36x10^4$
K Permanganate	$1.14x10^4$	525	$2.61x10^3$
K Dichromate	$2.61x10^4$	400	$1.48x10^3$
$Cu(II)(NH_3)_4^{2+}$	$2.90x10^3$	618	60
$Fe(III)SCN^{2+}$	$1.72x10^4$	469	$3.08x10^4$

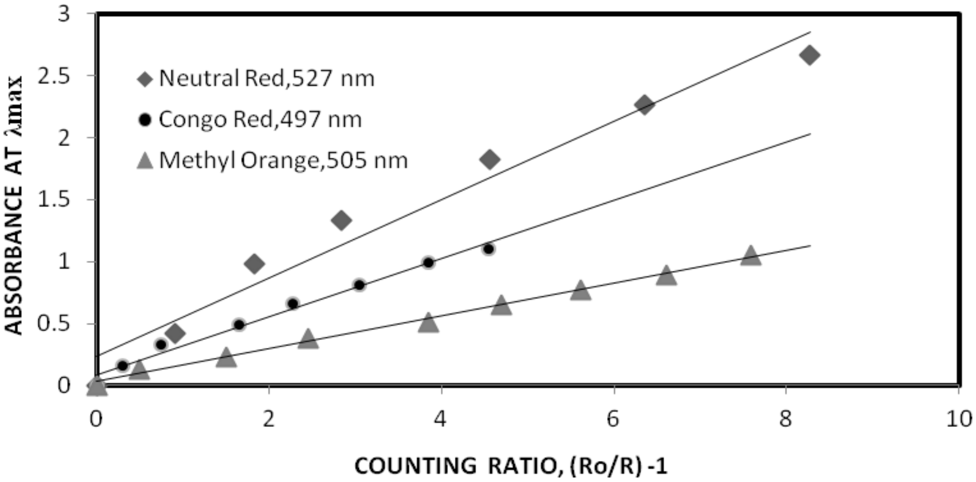

***Fig.3**. Correlations between visible light absorbances and Cerenkov light quenching ratios.*

At zero quencher concentration, counting efficiency E average out to 55%. Background data B has been determined before each series giving 55 CPM in average. In spite of a low value of so called Figure of Merit, (E^2/B) =55, it can be improved by increasing the KCl concentration and hence the counting efficiency E.

For random processes such as radioactivity, the 2σ error can be expressed as $2\sqrt{N}/N \times 100$, where N is the total net counts,(18). Therefore, an increase of KCl content in a factor of 2 or 3 will give 2σ error less than 10 percent. Another way to do this would be increasing counting time in order to improve the accuracy of data. Counting data were not influenced by inorganic potassium salts used as quenchers because of their low concentrations. As photometric technique it is suitable for organic or organometallic dyestuffs and a wide range of chemical analytes that exhibit color in aqueous solutions, including natural dyestuffs even though these are complex mixtures,(19).

***Table 2**. Parameters arising from Stern-Volmer relationships as calibration straight lines.*

Dye/Compound	Detection limit, p.p.m.	Linear range, p.p.m.	Linear regression coefficient
Malachite Green	1.9	13.9	0.9938
Murexide	7.9	56.0	0.9940
Brilliant Green	1.9	14.0	0.9970
Methylene Blue	1.9	14.0	0.9974
Methyl Orange	1.9	16.0	0.9979
Congo Red	2.0	14.0	0.9941
Methyl Red	1.9	14.0	0.9832
Neutral Red	3.9	24.0	0.9865
Eosin Y	1.9	11.9	0.9952
Bromophenol Blue	1.9	14.0	0.9920
Crystal Violet	31.0	----	--------
K Permanganate	1.9	14.0	0.9890
K Dichromate	2.0	14.0	0.9976
$Cu(II)(NH_3)_4^{2+}$	3.1	22.0	0.9882
$Fe(III)SCN^{2+}$	1.1	10.0	0.9976

Figure 4 illustrates K_{s-v} constants as a function of maximum of visible light absorbance wavelengths of chosen dyes or compounds, and resembles a spectrum. However, it only shows that Congo red is the best quencher of Cerenkov photons than the other ones.

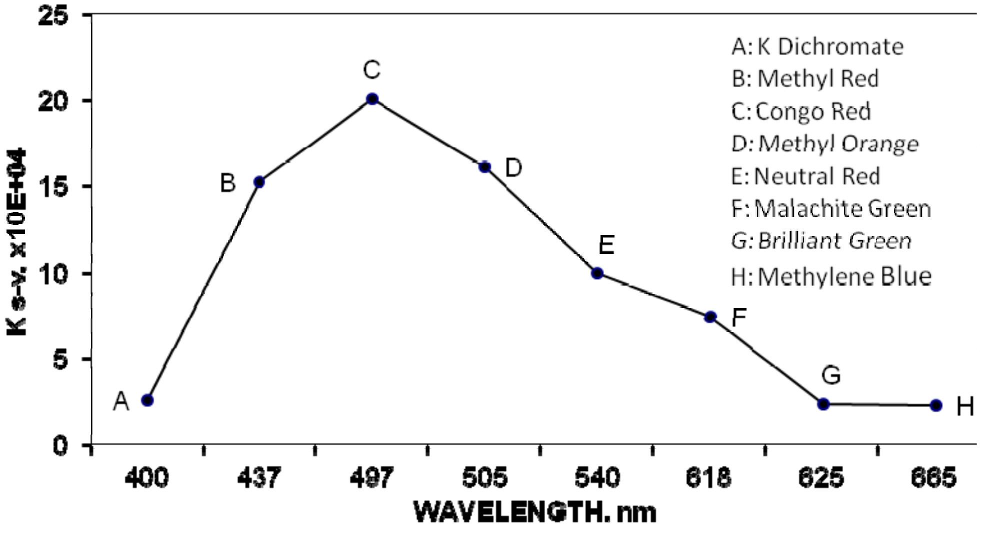

***Fig.4**. Stern-Volmer constants as a function of λ_{max} of selected dyes or compounds.*

On the other hand, Methylene blue and Brilliant green are worst quenchers. Cerenkov radiation as a shock wave, has a light frequencies composition larger toward the violet range. That is why the Cerenkov light is bluish in water. Experimental data show that blue solutions transmit blue light or does not quench it, and the other wavelengths are absorbed. Measurements of Cerenkov spectra for different radioisotopes by using color filters covering the interval 410-796 nm have been reported,(20). Different aqueous dye solutions working as filters could be another method to obtain the Cerenkov spectrum of ^{40}K . Among theoretical concerns about Cerenkov spectra fittings for reduced intensities in the near-ultraviolet region, a work has been published, (21).A reduction in Cerenkov radiation intensity can be caused by certain number of processes. Since the Stern-Volmer equation is obeyed , the main process involved is a collisional or dynamic quenching. In this case, electrons as fluorophores have contact with molecules of a dye or an inorganic anion. An important factor which contributes to the quenching phenomenon involves compounds with a high degree of conjugation that absorb visible or ultraviolet light. In the present case, Congo red has a large conjugated system than Crystal violet or Malachite green which are structurally related as substituted triphenylmetanes,(22). Since most of the tested dyes are acid-base indicators, it is important to take care pH conditions established experimentally.

EXPERIMENTAL SECTION

Cerenkov light due to beta emissions from ^{40}K were detected and counting rate measurements were carried out on a Liquid Scintillation Spectrometer Beckman 1800 at room temperature. Before routine counting, a program was activated on the instrument, in order to eliminate a warning concerning calibration and its performance was verified with Beckman standards of ^{14}C and tritium. For low activities, a Beckman calibration standard sample for background has been measured before each run. Beckman brand 20 mL vials of linear high density polyethylene were chosen because of low background. Polyethylene vials are suitable for this kind of measurements as was demonstrated in an earlier paper concerning counting efficiency,(23).

The liquid scintillation system consists of two photomultiplier tubes positioned face to face into a counting chamber provided with a reflector arranged in a very close 4π geometry. Electrical signal outputs from photomultipliers are connected to a coincidence and summing circuit. Events into a liquid sample that are sensed by both tubes within the resolving time are considered flash lights or scintillation pulses.

A detection response range was determined by using dissolved potassium chloride at different concentrations, up to 1.20 g KCl/10 mL water. Linear relationships between counting readings in counts per minute (CPM) and KCl contents were obtained.In order to assess counting rates, a concentration of 0.500g KCl/10 mL water was prepared as active solvent. Potassium chloride Riedel code 12636 and MiliQ quality water were used. The following dyes and compounds from Merck, Baker and Riedel were tested: Eosin Y, Brilliant green, Neutral red, Methyl red, Malachite green, Murexide, Bromophenol blue, Congo red, Methyl orange, Methylene blue, Crystal violet, Potassium permanganate, Potassium dichromate, Lead nitrate and Zinc nitrate. Complex ions such as $Fe(III)SCN^{2+}$ and $Cu(II)(NH_3)_4^{2+}$ were prepared in solution according to stoichiometric quantities. Acetonitrile, acetone, ethyl acetate and methanol, as pure solvents were also tested, adding volumes in the same amounts of dye solutions.

When measuring samples, background readings were mandatory in order to correct counting data and it has been made by counting 10 mL of pure water. Blanck samples or KCl solutions without any dye, gave counting rates Ro in counts per minute (CPM), after background corrections. Stock solutions of dye 0.1% in weight were prepared. Since dye purities are less than 100%, corrections have been made for every compound. To different vials containing 10 ml of KCl solutions, and by using an Eppendorf micropipette; a stock dye solution was added in increments of 20 µL up to160 or 180µL, then quencher concentration is progressively increased. In an other way, to a unique vial containing 10 mL of KCl solution; a dye solution was added using the above mentioned volumes. In the first case, each vial is counted separately and in the second one, only one vial is counted after an addition. Either serial samples or a vial in which concentrations are varied, gave same readings within experimental deviations. Counting rates were measured during one minute and repeated a minimum of three times. Furthermore, readings were only averaged without taking into account random variations because radioactive decay phenomenon, although instrument readings are accompanied by standard deviations σ. Standards and samples were handled into a shaded area because exposed vials to the direct sun light can cause counting rate variations. This effect has been verified with empty and filled vials.

A standard pH-meter provided with a glass-calomel electrode was used for measuring pH of solutions. Measured pH values were in the range from 5.50±0.20 at 20ºC. Dissolved oxygen has not been removed from solutions. Counted serial samples were also measured by visible spectrophotometry at their maximum absorbance wavelengths using a Spectronic model Helios Alfa double beam spectrophotometer. A pair of matched silica cells of 10.0 mm of optical path length was useful.

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