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Analyzing Electrochemiluminescence Signal and Detection Limits Through Device-Independent Color Space Mapping

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Summary:
Luminance quantification with consumer cameras becomes reliable through color space transformations, including gamma correction and conversion to device-independent spaces. This study offers an in-depth analysis of inter-channel relationships using the $Ru(bpy)_3^{2+}$/TPrA system as a model, demonstrating how distinct color dimensions reveal unique signal features. This approach improves noise assessment, detection limits, and overall robustness of smartphone-based ECL measurements, advancing their applicability in biosensing and diagnostics.

Keywords: Gamma correction, smartphone camera, image analysis, electrochemiluminescence (ECL), color spaces.

Background, Motivation and Objective

Smartphone cameras have become increasingly popular in analytical chemistry. Their portability, affordability, and advanced imaging capabilities have enabled widespread application in colorimetric, fluorescence, and chemiluminescence assays, particularly for point-of-care diagnostics [1-4].

Electrochemiluminescence (ECL), a light-emitting process initiated by electrochemical reactions, is especially well-suited for camera-based detection due to its high sensitivity, lack of background interference, and independence from external light sources [2]. However, the transition from traditional photodetectors to consumer-grade CMOS smartphone sensors presents new challenges. Mayor challenges are the nonlinear transformations introduced by the image signal processing pipeline—especially gamma correction—which distort the true relationship between recorded intensity values and analyte concentration [3,4].

Many studies still assume a linear response between RGB values and concentration, often neglecting the impact of device-specific encoding and perceptual distortions. This leads to significant errors in quantification, limiting the reproducibility and accuracy of such approaches [1-3].

This study evaluates how different device-independent color spaces (CIEXYZ, CIExyY, CIELAB) impact ECL quantification from smartphone images. By analyzing inter-channel relationships, signal variability, and detection limits, it shows that each color space reveals distinct signal characteristics. This multidimensional analysis improves accuracy and robustness for biosensing applications.

Description of the New Method or System

A smartphone-potentiostat-based ECL assay was combined with a standardized image processing workflow to quantify $Ru(bpy)_3^{2+}$/TPrA emission using RGB data transformed into CIEXYZ, CIExyY, and CIELAB color spaces. Beyond simple intensity measurements, the analysis explored inter-channel relationships such as a* vs. b*, hue angle, luminance (Y, L*), and chromaticity (xy), offering a multidimensional perspective.

Results

ECL emission, triggered by applying 1.2 V vs. Ag/AgCl, peaked around 5 s, marking the frame selected for analysis. RGB data were converted into device-independent color spaces (CIEXYZ, CIExyY, and CIELAB), enabling robust assessment beyond device limitations.

Quantification can be focused on red-sensitive channels—R (BT709), X (CIEXYZ), and a* (CIELAB)—using both linear (eq.1) and piecewise nonlinear models (eq.2) to capture signal response across concentrations (see Fig.1) [3].

$$Intensity = mC \quad (1)$$

$$Intensity = \begin{cases} b \cdot C, & C < T \\ c \cdot C^a - d, & C \geq T \end{cases} \quad (2)$$
$$with\ c = (b \cdot C\ + d)\ /\ (C^a)$$

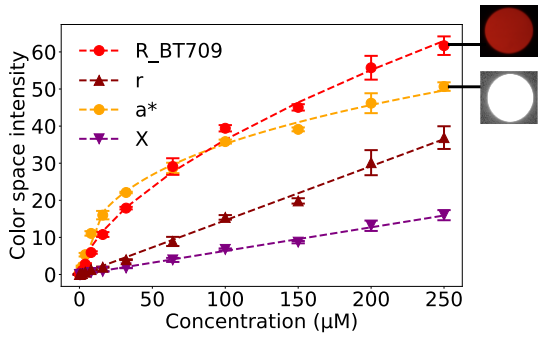

Fig. 1. Color space transformations of background-subtracted ECL intensity values from wavelength-selected channels relevant to the red-emitting ECL system, including R from BT709, linearized r, X from CIEXYZ, and a from CIELAB color space transformations.*

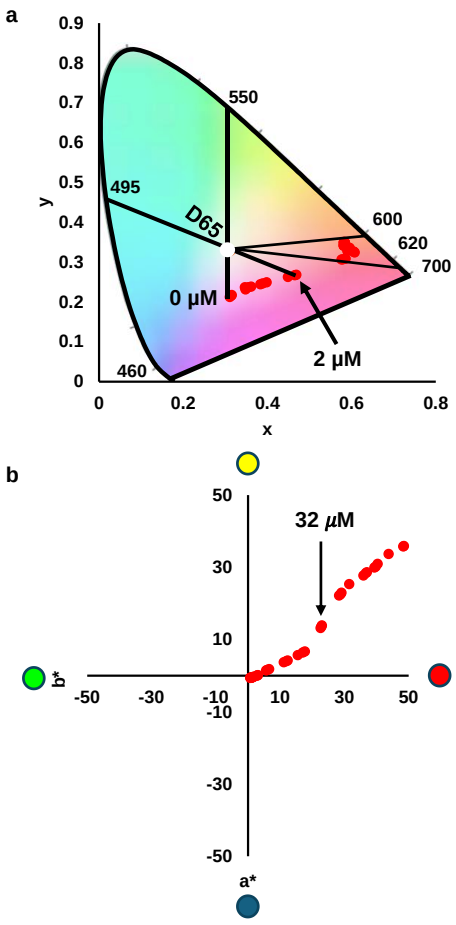

Fig. 2. a) CIExy chromaticity diagram showing ECL emission coordinates across concentrations, overlaid on the spectral locus, illustrating wavelength-related color shifts. b) CIELAB a vs. b* plot revealing chromaticity clustering behavior as a function of ECL intensity.*

Nevertheless, inter-channel studies revealed unique insights beyond intensity-based quantification. In the CIExy chromaticity plot (Fig. 2a), signal points below ~2 µM deviated from the expected chromatic locus red area, suggesting that the smartphone sensor lacks the resolution to reliably detect ultra-low concentrations without additional signal enhancement. Signal-to-noise ratio (SNR) and detection limit assessments across different color spaces confirmed ~2 µM as the practical threshold for reliable detection.

Meanwhile, the a* vs. b* plot (Fig. 2b) revealed two distinct signal regimes above and below ~30 µM, suggesting underlying shifts in emission characteristics that were not evident from intensity-only models

This multidimensional approach—combining color theory, inter-channel behavior, and perceptually relevant metrics—proves essential to capture both physical and visual attributes of ECL, supporting more accurate and interpretable quantification in biosensing applications.

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