Development and evaluation an alternative methodology for the quantification of dyes in fuels by photometry

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ABSTRACT

The detection and quantification of color in fuels is a practical method for the initial screening of quality and safety in these products. In this regard, researchers have been exploring alternatives for more effective and accurate color detection and quantification systems. This study aims to develop and evaluate a simple and cost-effective photometric methodology for quantifying color in colored fuels using a free software. The proposed technique is based on photographing the sample under standard conditions, with a calibration curve for each dye being measured by color intensity. Additionally, this work compares the proposed methodology with UV-visible spectroscopy to assess its effectiveness compared to other techniques. Preliminary results indicate that the proposed methodology is a viable alternative for the detection and quantification of dyes in fuels, showing good precision and reproducibility. Moreover, the technique can be employed in monitoring the quality of fuels available at gas stations, distributors and ethanol plants. This research makes an important contribution to the field of fuels by introducing a new technique for the detection and quantification of dyes in fuels.

RESUMO

A detecção e quantificação da cor em combustíveis é uma forma prática para triagem inicial de qualidade e segurança desses produtos. Nesse sentido, pesquisadores têm buscado alternativas de sistemas de detecção e quantificação de cores mais eficazes e precisos. Este estudo visou desenvolver e avaliar uma metodologia fotométrica simples e de baixo custo para quantificação de cor em combustíveis coloridos, utilizando software livre, como alternativa à simples análise visual direta. A técnica proposta baseia-se na fotografia da amostra em condições padrão, sendo a curva de calibração para cada corante medida pela intensidade da cor. Adicionalmente, este trabalho compara a metodologia proposta com espectroscopia UV-visível, a fim de avaliar sua eficácia em relação a essa técnica. Os resultados preliminares indicam que a metodologia proposta é uma alternativa viável para a detecção e quantificação de corantes em combustíveis, apresentando boa precisão e reprodutibilidade. Além disso, a técnica pode ser utilizada na fiscalização da qualidade dos combustíveis disponíveis nos postos, no recebimento de matérias primas em distribuidoras e usinas de etanol anidro. A pesquisa apresenta uma interessante contribuição para a área de combustíveis, descrevendo uma técnica quantitativa simples de detecção e quantificação de cor em combustíveis.

INTRODUCTION

In recent years, the oil sector in Brazil has been implementing increasingly stringent regulations, demanding products of higher quality [1]. The Fuel Quality Monitoring Program (PMQC - Programa de Monitoramento da Qualidade de Combustíveis) aims to monitor the overall quality of fuels sold in Brazil in order to detect the presence of products that do not meet the technical specifications established by the National Agency of Petroleum, Natural Gas, and Biofuels (ANP - Agência Nacional do Petróleo, Gás Natural e Biocombustíveis). One of its main goals is to identify points of non-compliance, with the purpose of guiding and improving enforcement activities in the fuel supply sector of the Agency.

Fuels are complex matrices obtained through different refining processes, in addition to receiving the addition of other chemical compounds [2]. To ensure the quality of fuels, distributors use markers to control the origin and quality of their products and to combat potential fraud and adulteration [3]. These markers can be dyes, specifically known as marker dyes. The importance of using marker dyes lies primarily in maintaining the individuality and characteristics of each product [4].

In January 2002, the ANP implemented the Compulsory Marking Program for Products. Currently, Resolution ANP No. 902/2022 establishes the necessary requirements for the registration of companies interested in supplying marker products.

In the field of fuels, markers are defined as substances that, when added to solvents or petroleum derivatives, do not alter their physicochemical characteristics, and do not interfere with the safety level during handling and use. These markers can be identified using specific analytical methods [5].

Among them, the most sophisticated methods stand out, such as the use of non-radioactive isotopes, chromatographic techniques, and spectroscopic techniques. Although these quantification techniques are highly sensitive to small variations in concentration, they are associated with high acquisition and maintenance costs [6,7]. Therefore, the market needs tools that are easy to apply, cost-effective, and reproducible.

The methodology proposed in this study is based on photographing the sample under standard conditions, with the calibration curve for the dye being measured by color intensity. The focus on this paper was the quantification of the orange dye in Anhydrous Ethanol Fuel (AEF) but we also tested this methodology for green dyes like the ones used in gasoline and hydrous fuel ethanol sold in Brazilian gas stations. The main objective of the proposed methodology is its application in mobile laboratories, and screening test of raw materials in fuels terminals, providing color analysis as a quantitative tool. Additionally, this study establishes a comparison with UV-Vis spectroscopy method, which is a widely recognized tool for dye quantification in the literature.

QUANTIFICATION OF DYES

According to ANP Resolution 907/2022, the dye added to the AEF must be orange, totally soluble in anhydrous ethanol fuel and totally insoluble in water at a concentration of 15 $mg.L^{-1}$ [8]. This resolution specifies the monitoring of the orange dye present in the AEF, at wavelengths of 420 nm and 530 nm.

It is important to note that the literature presents a limited collection of works involving markers in fuel samples, the majority of which are protected by patents [9]. The detection and quantification of dyes in fuels are crucial to ensure the quality and safety of these products, and also inhibits fraud resulting from blending with lower-taxed products.

Researchers have been seeking alternative color detection and quantification systems that are effective and precise. The detection technique used is linked to the chemical structure of these compounds. Marker dyes are organic compounds with aromatic resonance [10]. These markers are added to fuels to allow for visual distinction [11]. Synthetic dyes are categorized based on their characteristics and applications, following a general naming pattern: "solvent + color + number" [1].

These dyes are insoluble in water and highly soluble in petroleum-derived hydrocarbons, and they should not alter the physicochemical properties of the fuels in which they are inserted. They should also exhibit relative resistance when subjected to usual removal techniques [12]. The purpose of marking with these dyes ranges from preventing tax fraud to environmental protection, allowing differentiation of fuels with high sulfur content.

The two main groups of dyes are those containing azo functional groups and those containing anthraquinone functional groups [13]. The presence of polar and nonpolar substituents, along with electron-donating atoms to the aromatic ring, provides a conjugated electron-delocalization system [14]. The chemical structure of the dyes allows for the absorption of radiation in the visible region and makes these substances suitable for detection by various analytical techniques, including spectroscopy and chromatography [11,12].

Visual methods are simple but do not offer analytical reliability, mainly because they do not differentiate small variations in color [15] and may be subjected to environmental conditions carrying a strong interobserver error. Spectrophotometric methods with absorption in the ultraviolet and visible regions are simpler, cost-effective, and relatively easy to perform. However, they are challenging to apply in mobile units. The market requires effective and low-cost tools that can be applied in different stages of the production chain.

MATERIALS AND METHODS

PREPARATION OF STANDARD SOLUTIONS – The standard solutions were prepared using the orange dye, Dorf Solvent Orange EGB, in anhydrous ethanol fuel. The Color Index codes and formulation of the dyes used are not disclosed for confidentiality reasons. The solutions were prepared at concentrations of: 2.5 $mg.L^{-1}$; 5 $mg.L^{-1}$; 7.5 $mg.L^{-1}$; 10 $mg.L^{-1}$; 12.5 $mg.L^{-1}$; 15 $mg.L^{-1}$; 17.5 $mg.L^{-1}$; 20 $mg.L^{-1}$; 22.5 $mg.L^{-1}$ e 25 $mg.L^{-1}$, with a final volume of 100 mL each. The solutions were stored in polystyrene bottles and no precipitate formation was observed during the preparation process.

UV-VIS SPECTROSCOPY – The Genesys 180 UV-Vis instrument was used for UV-Vis spectroscopy. The UV-Vis spectra were collected in the range of 300 nm to 700 nm with a resolution of 1 nm. The optical path length was set to 10 mm, and a data acquisition time of 10 seconds was used. The blank measurement was obtained using anhydrous ethanol fuel. The data were processed using Microsoft Excel 365. The wavelengths monitored for the construction of the calibration curve were 420 nm and 530 nm. The measurements were performed in triplicate, and readings were taken with an empty cuvette for the blank.

PHOTOMETRY - The images were captured using a Samsung Galaxy A51 smartphone with the default capture mode, at a fixed distance of 25 cm from the color chart. The color intensity data were obtained using the free software ImageJ [16]. For data collection, a color chart (Figure 1) was used. The chart had marked areas for selection, indicated the position of the sample-containing beaker, and included red, green, and blue color standard patches.

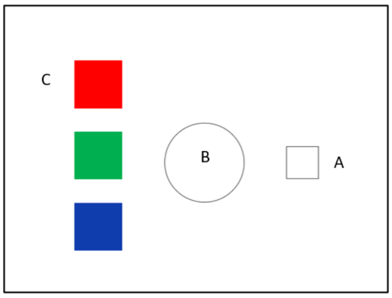

Figure 1. Template used for photography. (A) Marking of the selection area; (B) Position of the beaker containing the sample. (C) Red, green, and blue color standard patches.

The ImageJ software quantifies the color intensity of the selected area, with the maximum color intensity of 255 for the white color. The data obtained in this study were processed in Microsoft Excel 365, including the construction of the presented graphs. No photographic studio or flash was used for capturing the photographs. The measurements were performed in triplicate. For each point on the calibration curve, the color intensity value of the white reference was subtracted.

VALIDATION OF THE METHODOLOGY – The concentration of the Dorf Solvent Orange EGB dye in Anhydrous Ethanol Fuel was calculated for both the Photometric and Spectrophotometric methods using the calibration curve and linear regression analysis for methodology validation.

RESULTS AND DISCUSSION

SPECTROSCOPY EVALUATION - The calibration results of the standards can be observed in Figure 2. The wavelengths monitored in the spectrophotometry are those specified in ANP Resolution No. 907/2022, at 420 nm and 530 nm.

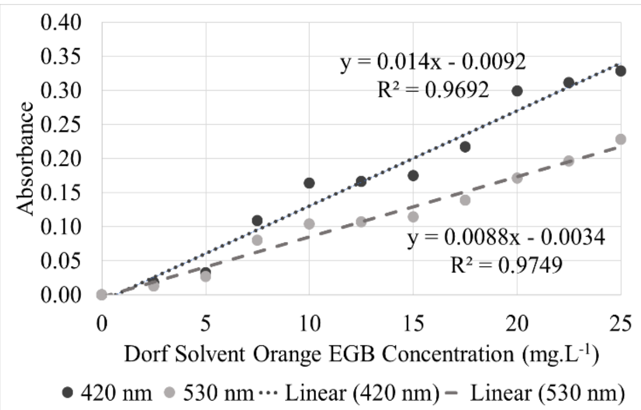

Figure 2. Calibration curve using Dorf Solvent Orange EGB dye for the spectrophotometric method in the concentration range of 2.5 mg.L^{-1} to 25.0 mg.L^{-1}.

Upon analyzing the investigated samples, we noticed that, even at different wavelengths, they exhibited a similar pattern in the overall distribution of the data. This observation led us to identify a sudden uniformity of the data within the concentration range of 7.5 to 10 mg.L^{-1}, suggesting a correlation with an intrinsic behavior of the dye used.

The ANP Resolution No. 907/2022 establishes the absorption monitoring intervals of 0.150 to 0.190 for 420 nm and the absorption range of 0.100 to 0.135 for 530 nm for a concentration of 15 mg.L^{-1}. The presented data are in accordance with the resolution (Figure 3).

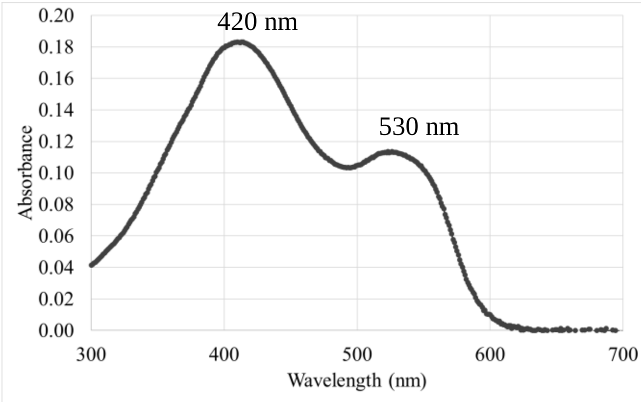

Figure 3. UV Absorbance Curve of Anhydrous Ethanol Fuel at 15 mg.L^{-1} of Dorf Solvent Orange EGB dye for the spectrophotometric method in the wavelength range from 300 nm to 700 nm.

PHOTOMETRY EVALUATION – By using the template shown in Figure 4, the results indicated in Table 1 were identified. These results correspond to a calibration standard of the software used to measure the values obtained by photometry.

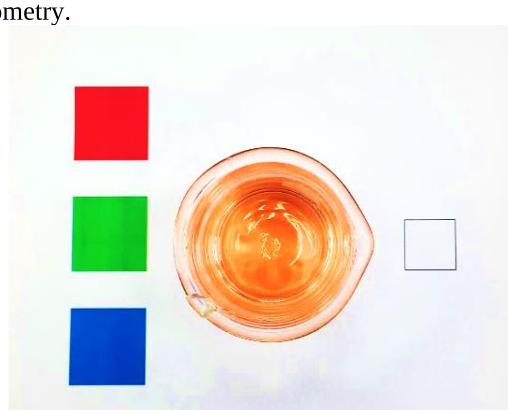

Figure 4. Image of the photometric method at a concentration of 15 mg.L^{-1} for the Dorf Solvent Orange EGB dye.

Using the software configured with the measurements described in Table 1, it was possible to measure the color intensity data shown in Figure 5.

Table 1. Quantification for the color standards of the template using the Photometry method. Average of 10 measurements of the blank. (RSD) Relative Standard Deviation.

	Color Standards		
	RED	GREEN	BLUE
Average	94.53	67.98	69.81
RSD	10.60	7.06	10.13

By analyzing the graph in Figure 5, a similar variation was observed, as evidenced in the spectroscopy measurements, at the corresponding points of 7.5 and 10mg.L^{-1}. These results support the initial hypothesis of a possible discrepancy in coloration with increasing concentration.

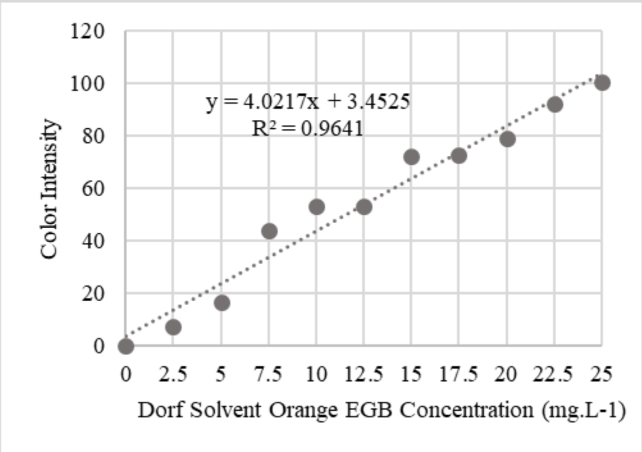

Figure 5. Calibration curve using the Dorf Solvent Orange EGB dye for the photometric method in the concentration range of 2.5 mg.L^{-1} to 25.0 mg.L^{-1}.

METHOD VALIDATION - The results shown in Figure 6 were obtained by interpolating the data of Absorbance at 530 nm and Color Intensity using the Concentration of Dorf Solvent Orange EGB dye as an intermediate variable in this association. It is important to note that, due to its better fit to the curve, only the data of Absorbance at 530 nm were used, as evidenced by the coefficient of determination (R^2).

The RANP 907 of 2022 demands a fixed concentration of 15 mg/L^{-1}. The results obtained at this point using the spectrophotometric method show a slight deviation from the linear correlation, while for the photometric method, this deviation is less evident. The deviation from the linear correlation suggests factors associated with weigh the dye and dilution for the construction of the calibration curve or matrix behavior at this concentration.

In accordance with the data presented above, a linear relationship can be observed between the axes, with a coefficient of determination (R^2) of 0.9617. This statistically indicates a low variability of the results in relation to the regression line. These results demonstrate a good fit of the photometric methodology compared to spectroscopy using absorbance at 530 nm as the parameter.

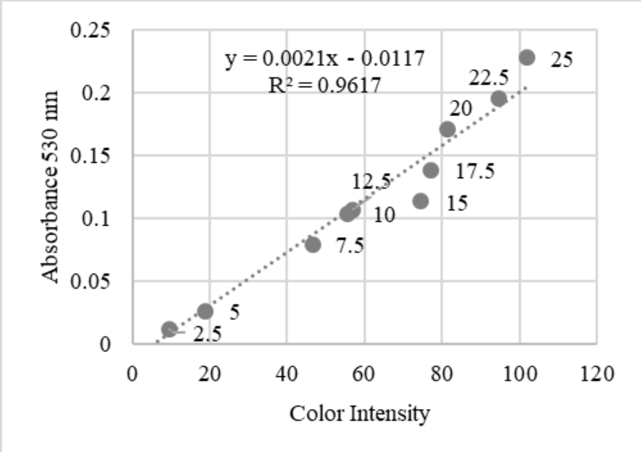

Figure 6. Interpolation of the Absorbance at 530 nm and Color Intensity methodologies.

The alternative photometric methodology presented in this study was also applied to quantify a green dye in Hydrous Fuel Ethanol. The linear working range showed an R^2 value of 0.9954 with a relative error of less than 10% demonstrating the potential use of this fast and cheap color quantification method for different dyes and fuels. The expense for analysis the Photometric method is approximately 1% the regulated method. The calculation of the expense for analysis, evaluates expenses with materials, analysis time, maintenance, and calibration of the equipment. The proposed methodology is currently under experimental use by Vibra Energia for identifying typical production values of Anhydrous Ethanol Fuel, as well as other colored products.

CONCLUSIONS

In this study, an alternative methodology for the quantification of dyes in fuels using photometry was developed and evaluated. This low-cost tool can be applied at various stages of the production chain. It is important to note that this tool does not replace existing methods specified in standards; rather, it serves as an additional tool for quality analysis and preliminary identification of non-conformities. The results demonstrate a good correlation between the alternative photometric methodology and spectroscopy. This work can serve as a basis for further studies involving different fuel formulations, such as avgas and Diesel S-500.

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