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Determination of Ethanol in Wine and Distilled Alcoholic Beverages Using a Smartphone as a Detector

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Abstract: This paper describes the application of a smartphone as a detector in the determination of ethanol in distilled beverages. Digital image analysis as an analytical tool is a reality nowadays, and the use of smartphones stands out due to its high accessibility and practicality. The aim is to determine ethanol in distilled beverages using two cheap and simple methods using a smartphone as a detector. Two methods were used, with phenanthroline (method A) and with potassium dichromate (method B) as a reagents and two detectors, spectrophotometer and smartphone. Linear dependence of signal was achieved in the concentration range: from 1.0 to 65.0% (v/v) for method A and from 7.0 to 50.0% (v/v) for method B. The concentration range that is linear with the signal is wide and allows sufficient sensitivity and thus gives the possibility to determine a variety of distilled beverages. Comparison of the obtained results shows that the smartphone and the proposed reagents can be used in routine analysis in quality control of used samples. The results obtained are comparable with the results obtained using a spectrophtometer or with nominal values. The method proved to be simple and inexpensive for the determination of ethanol, does not use expensive reagents neither laborious procedures to carry out the analysis.

Keywords: Ethanol Determination, Smartphone Detector, IT Technologies in Chemistry

1. Introduction

Ethanol is an integral part of all alcoholic beverages in which it is formed by fermenting sugar with the help of yeast. Alcohol is used as a solvent (well dissolves fats, oils and dyes) and a means for extraction, disinfection, preservation and for the production of artificial alcoholic beverages. For large industries, as well as small ones engaged in the production of alcoholic beverages, the goal is to determine the percentage of ethanol in the simplest possible way. There are several methods for determining the concentration of ethanol in alcoholic beverages, and they are mainly divided into physical, chemical and enzymatic. In routine analysis, as in the beverage industry, ethanol is usually separated from the matrix by a distillation process, and only then by a physical or chemical method [1]. Nowadays, simple analysis of alcohol using a smartphone is gaining more and more attention, because the results are obtained much faster than, for example, using a spectrophotometer [2]. The aim of this paper is to determine ethanol using a smartphone, and then test the application of the method in the analysis of real samples (commercial and domestic alcoholic beverages). Based on the obtained results, an attempt will be made to show the possibility of replacing the spectrophotometer with a smartphone.

The revolution of today's smartphones has reached its "peak", so the quality of the digital camera itself has improved. Digital camera resolution is expressed in megapixels. A pixel is a basic image element, typically stored in 24-bit resolution that is further divided into three 8-bit groups. Each of these 8-bit groups corresponds to one color; red, green and blue. The human eye possesses 3 types of conical cells that recognize only three different colors: red, blue, and green. This phenomenon is called tricolor vision, so dividing it into three primary colors is sufficient instead of storing the entire spectrum [3-5].

Gas chromatography (GC) is one of the common methods for determination of ethanol concentration in alcoholic beverages due to its accuracy, and sensitivity [6-8]. However, this method requires expensive instrument and skilled worker for analysis. In addition, one instrument could analyze one sample at a time of analysis. Distillation is one of the selected choices for factory's lab, although it is time-consuming, and laborious [9]. Distillation and mass determination show less accuracy due to the presence of interfering volatile or other components in samples [10]. determination of ethanol by titration with potassium dichromate in an acid condition that the color change of redox reaction was observed as the endpoint [11]. The spectrophotometric method had been developed using the reaction of potassium dichromate in concentrated acid and ethanol to produce chromium (III) and acetic acid and then was spectrometrically measured. The reaction is completed in 15 min at room temperature and the chromium (VI) consumed can be determined by the decrease of absorbance at 267 nm [12]. The widely used method are also gas chromatography-mass spectrometry [13], liquid chromatograph-mass spectrometry [14], infrared spectrometry with partial least squares regression [15], fluorimetric [16], amperometric [17], potentiometric [18] and (bio)-sensors, or redox titration with potassium dichromate [19].

Colorimetric detection for chemical analysis was reported as an alternative method for a spectrophotometer. Using Charge Coupled Device (CCD) and Complementary Metal Oxide Semiconductor (CMOS) devices from a digital camera [20], web camera [21], smartphone camera [22, 23] and scanner [24] were achieved with RGB color model for signal processing in RGB intensity. Measurements based on digital images have incorporated clear advances to analytical procedures, especially in relation to practicality, analytical productivity, simplicity, exploitation of low-cost instrumentation, and minimal waste generation. Procedures based on digital images have been applied for determinations ethanol [2, 25] in beverages.

The aim of this paper is to determine ethanol in distilled beverages using two cheap and simple methods using a smartphone as a detector.

2. Materials and Methods

2.1. Chemicals, Reagents and Samples

All reagents used were of analytical reagent grade and were purhased from Sigma Aldrich. Water used for preparation of solution was Milli Q (18,3 M Ω cm^{-1}).

Stock solution of potassium dichromate and phenolphthalein were prepared by disolving appropriate amount of these substances in ultra pure water and ethanol, respectively. The ethanol stock solutions for calibration procedure were prepared by diluting concetrated ethanol (96% v/v) in ultrapure water.

A stock solution of 1.0% (w/v) phenolphthalein was prepared in 65.0% (v/v) ethanol. The working solution of phenolphthalein (0.1%, w/v) was prepared by diluting stock solution in 50% (v/v) ethanol.

The stock solutions were prepared weekly.

The alcoholic drink samples were purchased in local supermarkets and analysed without prior processing.

2.2. Apparatus

Spectrophotometric measurement was procesed ba using UV 1800 Shimadzu double beam spectrophotometer equipped with quarz cells of 1 cm path width.

Samsung Galaxy s10+ camera, was used for digital images capturing. The camera of this device has 2MP wide-angle lenses (77°) with a double aperture and double pixels. It also includes built-in optical image stabilization (OIS) software to reduce image blur.

2.3. Method with Phenolphthalein as Reagent

Reaction solutions were prepared acording to a previously published method that has been slightly modified [26].

In reaction cuvete were aded 2 mL of sample/standard, 4000 µL of reagent (0.1% w/v phenolphthalein) and 100 µL 0.1 mol L^{-1} NaOH.

Standard solution of ethanol for preparation of calibration curve in concentration range from 1.0 to 65.0% (v/v) were prepared by diluting concentrated ethanol (96.0%, v/v).

For all reaction solution measurements of absorbance was performed with a spectrophotometer at a wavelength of 580 nm. Smartphone was used for capturing a digital picture of reaction solution in controled conditions. All measuremments were performed in triplicate. RGB software Gimp 2.10 (Google play app) was used for digital image processing and determination of intensity of G values.

2.4. Method with Potassium Dichromate as Reagent

For procedure and preparation of reaction solutions were run acording to a previously published method that has been slightly modified [27]. Reaction solutions were prepared by mixing 640 µL of sample or standard, 2560 µL of 0.05 mol L^{-1} potassium dichromate and 140 µL of concentrated sulfuric acid solution. Ethanol solutions in the concentration range from 7.0 to 50.0% (v/v) were used for preparation of the calibration curve. Measurements of absorbance are performed with a spectrophotometer at a wavelength of 535 nm. For the same solution are captured digital images by smartphone.

All measuremments were performed in triplicate.

2.5. Photographic Procedure

Reaction solutions with standard or sample were placed in a quartz cuvette for spectrophotometric measurements. During the image capture cuvette were placed in front of a white background. The images were acquired using ambient lighting and the smarphone was firmly placed in the front part, at a distance of 12.0 cm from the cuvette. During imaging, direct light was always directed from the cell phone's LED flashlight.

The captured images were analysed by using free RGB software GIMP 2.10. Intensity of R, G and B canels were furter processed by Microsoft Excel.

It is necessary to select the region of interest for the cuvette image for which the software will calculate the RGB intensity. The RGB intensity for white background in each captured image mast be compared because of consistency of the measurement.

3. Results and Discussion

Phenolphthalein is known as an acid-base indicator that is colorless in an acidic medium, but at a pH value greater than 8.3 it turns pink.

Also, discoloration of the alkaline solution of phenolphthalein was observed with the addition of ethanol. In this paper, the decrease in the pink color intensity of the solution of this indicator due to the increase in ethanol concentration was used for the quantitative determination of ethanol in distilled beverages.

Also, the another one colorimetric reaction with potassium dichromate in acidic medium was used for determination of ethanol:

$$Cr_2O_7^{2-} + H^+ + 3\,CH_3CH_2OH \leftrightarrow 2\,Cr^{3+} + 3\,CH_3CHO + 7\,H_2O$$

The method is sensitive and the reaction solutions with ethanol were colored at yelow to green-blue depending on the ethanol concentration. The measurement must be made at a fixed time interval after the addition of the reagent. Diffrent signal uptake times were tested and it was found that the best sensitivity is achieved in a time of 12 minutes.

Analytical Application

Measurements were made under the described conditions and a linear relationship between signal and concentration was achieved in the range of 1.0 to 65.0% (v/v) for the phenolphthalein method and for dichromate method linear dinamic range was from 7.0 to 50.0% (v/v). The results obtained using the smartphone were approwed using a spectrophotometer and the same linear responses were achieved. Direction equations, and correlation coefficients are given in Table 1.

No analytical signal differences greater than 3.0% were observed during interference testing. An ethanol standard solution with a concentration of 40.0% (v/v) was used at the interfernence testing, and sugars (fructose, glucose, sucrose) up to a concentration of 40 mg L^{-1} and sulfite up to 40 mg L^{-1} were tested. Alcohols of ethanol-like structure may be interferences, but should not be present in beverages. Furthermore, intensely colored distilled beverages also cannot be analyzed by the applied analytical methods.

For both methods used, an increase in G channel intensity was observed with increasing ethanol concentration. Also, a wider range of concentrations and better sensitivity were achieved with the G channel, and due to all the above, this channel was used for the calibration line.

Equation of obtained calibration lines, coefficient of correlations, limits of detection, the linear range of concentration all obtained by two methods were given in Table 1.

The concentration range that is linear with the signal is wide and allows sufficient sensitivity and thus gives the possibility to determine a variety of distilled beverages.

Table 1. *Concentration range obtained with two applied methods, equation of calibration lines, the limit of detection (LOD), and coefficient of correlation (R^2).*

	Concentration range,% (v/v)		Equation of calibration line	LOD,% (v/v)	R^2
Ph. method	1.00 – 65.0	Spectroph.	A = -0.015 x + 1.112	0.70	0,999
		Smartph.	G = 1.976 x + 27.595		0.994
Dichr. method	7.0 – 50.0	Spectroph.	A = 0. 0371 x + 0, 4287	5.0	0.997
		Smartph.	G = 0. 7034 x + 56. 623		0.993

Ph.- phenanthroline; Dichr.-dichromate; Spectroph.-spectrophotometry; Smartph.-smartphone A-apsorbance; G-G channel; x-concentration of ethanol,% (v/v).

Also, commercially available samples were analyzed, and the results obtained using a smartphone were compared with the results obtained spectrophotometrically and with nominal values (Table 2 and Table 3).

The applied methods are effective in the analysis of real samples regardless of whether a mobile phone or a spectrophotometer is used as a detector.

The analysis does not require significant time consumption. A simple procedures and chemicals available to most laboratories were applied, small volumes of chemicals were consumed and waste generation was reduced.

Table 2. *Comparison of results obtained in the analysis of commercial distilled beverages by using method with phenolphthalein.*

Sample	Nominal (%, v/v)	Spectrophotometer		Smartphone	
		Found (%, v/v) ± SD	Recovery,%	Found (%, v/v) ± SD	Recovery,%
Vodka Romana	40.0	41.01±1.25	102.5	38.95±0.99	97.4
Vodka Vigor	37.5	38.50±0.98	102.7	39.55±1.27	105.5
Vodka Cosmopolitan	37.5	36.20±0.97	96.5	39.15±0.74	104.4
Ballantines	40.0	40.46±0.84	101.2	39.74±0.40	99.3
Viljamovka	40.0	40.39±0.41	101.0	39.55±1.01	98.9
Plum brandy	40.0	40.20±0.97	100.5	41.03±0.51	102.6
Grape brandy	40.0	41.17±0.96	102.9	40.87±0.72	102.2

Table 3. *Comparison of results obtained in the analysis of commercial distilled beverages by using method with potassium dichromate.*

Sample	**Nominal (%, v/v)**	**Spectrophotometer**		**Smartphone**	
		Found (%, v/v) ± SD	**Recovery,%**	**Found (%, v/v) ± SD**	**Recovery,%**
Vodka Romana	40.0	40.44±0.98	101.1	40.71±0.96	101.8
Vodka Vigor	37.5	38.35±0.89	102.3	38.44±1.11	102.5
Vodka Cosmopolitan	37.5	38.92±0.92	103.8	39.15±0.99	104.4
Ballantines	40.0	40.85±0.95	102.1	39.74±0.97	99.3
Viljamovka	40.0	41.35±1.22	103.4	41.08±1.35	102.7
Plum brandy	40.0	39.27±0.56	98.2	40.43±1.05	101.1
Grape brandy	40.0	41.07±0.62	102.7	38.87±0.92	97.2

4. Conclusions

The method has shown satisfactory applicability in the analysis of real samples. Conditions were optimized: pH, volume of added reagent, volume of added analyte, possible interferences were tested. It has been shown that two simple and inexpensive methods that use a smartphone as a detector can be used in the analysis of distilled beverages and that the results obtained are comparable with the results obtained using a spectrophtometer or with nominal values.

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