

วิธีวิเคราะห์โซเดียมอย่างง่ายด้วยโฟโตแกรมเมตรี

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จุดประสงค์หลักของงานนี้ คือ การศึกษาความเป็นไปได้ที่จะใช้ภาพจากกล้องดิจิทัลมาวิเคราะห์จุดภาพแล้วเปลี่ยนบริเวณจุดภาพที่สนใจเป็นอาร์เรย์ตัวแทนเพื่อตรวจหาปริมาณโซเดียมในเครื่องต้มทดแทนเกลือแร่ วิธีนี้เป็นวิธีการเกี่ยวกับการวิเคราะห์ภาพถ่ายดาวเทียมโดยรีโมตเซนซึ่งเรียกว่า “โฟโตแกรมเมตรี” วิธีที่นำเสนอนี้ง่าย ใช้เครื่องมือราคาถูกและมีความไวสูง **วัสดุและวิธีทดลอง:** วิธีที่นำเสนอมีพื้นฐานจากการนำสารละลายมาตรฐานและตัวอย่างเข้าสู่เปลวไฟที่เกิดจากอากาศผสมอะเซทิลีน ภาพของเปลวไฟจะถูกบันทึกด้วยกล้องถ่ายภาพแบบดิจิทัล ภาพของเปลวไฟที่ได้จากสารละลายมาตรฐานและตัวอย่างเครื่องต้มทดแทนเกลือแร่จะนำไปผ่านกระบวนการเพื่อเปลี่ยนระดับสีและความสว่างให้เป็นค่าความเข้มด้วยโปรแกรมที่พัฒนาขึ้น วิธีการอ่านค่าระดับสีและความสว่างนี้ได้นำไปประยุกต์ในการหาปริมาณโซเดียมในตัวอย่างเครื่องต้มทดแทนเกลือแร่ และได้เปรียบเทียบวิธีดังกล่าวนี้กับวิธีเฟลมอะตอมมิกอิมมูเนสเซนซ์สเปกโทรโฟโตเมตรี **ผลการศึกษา:** กราฟมาตรฐานของสารละลายมาตรฐานโซเดียม ให้ค่าความเป็นเส้นตรงในช่วง 0.4 – 2.0 ไมโครกรัมต่อมิลลิลิตร มีค่าสัมประสิทธิ์สหสัมพันธ์ของความเป็นเส้นตรง 0.9901 ($n=5$) ค่าขีดจำกัดการตรวจวิเคราะห์ (LOD) และขีดจำกัดการบ่งปริมาณ (LOQ) โดยมีข้อกำหนดพื้นฐานของสัญญาณที่วัดเทียบกับสัญญาณรบกวน ในอัตราส่วน 3:1 และ 10:1 ตามลำดับ ค่าขีดจำกัดการวิเคราะห์และขีดจำกัดการบ่งปริมาณ คือ 0.12 และ 0.38 ไมโครกรัมต่อมิลลิลิตรตามลำดับ มีการศึกษาผลการรบกวนที่เป็นไปได้จากน้ำตาล(กลูโคส เดกซ์โทรส และซูโครส)และ ไอออนรบกวน(K^+ , Zn^{2+} และ Mg^{2+})ในการวิเคราะห์โซเดียม พบว่าผลการรบกวนจากน้ำตาลและไอออนที่ศึกษามีอิทธิพลต่อสัญญาณน้อยกว่า $\pm 2.5\%$ **สรุปผล:** ได้พัฒนาวิธีโฟโตแกรมเมตรีอย่างง่ายที่ใช้ในการวิเคราะห์ปริมาณโซเดียมในตัวอย่างเครื่องต้มทดแทนเกลือแร่ขึ้น วิธีโฟโตแกรมเมตรีที่นำเสนอนี้ได้เปรียบเทียบกับวิธีเฟลมอะตอมมิกอิมมูเนสเซนซ์สเปกโทรโฟโตเมตรี ซึ่งผลการศึกษาที่ได้ไม่แตกต่างกันด้วยความเชื่อมั่นที่ระดับ 95% โดยใช้สถิติ t -test วิธีที่ได้นำเสนอนี้เป็นวิธีที่มีขั้นตอนที่ง่ายและค่าใช้จ่ายที่ต่ำ

คำสำคัญ: โซเดียม, โฟโตแกรมเมตรี, ภาพดิจิทัล, เครื่องต้มทดแทนเกลือแร่

Simple Method for Determination of Sodium Using Photogrammetry

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Abstract

Simple Method for Determination of Sodium Using Photogrammetry

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The main purpose of this work is to study the possibility of using digital image from camera and convert array of pixels as matrix for determination of sodium in sport drink samples. This method is also used in satellite image processing by remote sensing called "Photogrammetry". The present method is simple, inexpensive instrumentation and rapid process with high sensitivity. **Materials and methods:** The proposed method is based on aspirated the standard or sample solution into a burner that ignites flame by mixing fuel between air and acetylene. Digital images of flame emission were recorded using digital camera. Images of the flame emission from standard sodium solution and sport drink samples were processed to read the pixels array color which was converted to concentration using in-house program. The pixels array reader method was applied to quantification sodium from sport drink samples and the results were compared to the flame atomic emission spectrophotometric method. **Results:** The calibration curve for standard sodium solution shown an excellent linearity over a concentrations range of 0.4 – 2.0 $\mu\text{g mL}^{-1}$. The correlation coefficient was obtained to be 0.9901 ($n=5$). The limit of detection (LOD) and the limit of quantitation (LOQ) were determined based on the criteria of signal-to-noise ratio for LOD and LOQ are 3:1 and 10:1, respectively. The results of LOD and LOQ were found to be 0.12 and 0.38 $\mu\text{g mL}^{-1}$, respectively. Effects of some possible flavor sugars (glucose, dextrose and sucrose) and interfering ions (K^+ , Zn^{2+} and Mg^{2+}) on the determination of sodium were also investigated. All of flavoring sugars and metal ions interfered the monitoring signal in the range below $\pm 2.5\%$. **Conclusion:** A simple method for determination of sodium in sport drinks was developed using photogrammetry. The proposed photogrammetric method and flame atomic emission spectrophotometric method showed positive agreement with no statistical difference at 95% confidential level by the *t*-test. The study demonstrated potential of photogrammetry beyond simple procedure and cost-effective method.

Keywords: Sodium, Photogrammetry, Digital image, Sport drinks

Introduction

Sport drinks are specifically designed for, or marketed towards, people who are undertaking physical activity, being mainly composed by carbohydrates, electrolytes and vitamins. One typical ingredient was sodium chloride salt. High salt content can be harmful to health because it increases of the blood pressure with age related with the risk of hypertension (Havas *et al.*, 2007) and cardiovascular disease (Campbell *et al.*, 2011). An increasing correlation exists between high salt intake and the risk of overweight (Song *et al.*, 2013). World Health Organization (WHO) recommends reducing sodium intake to < 2g/day (5g/day salt) (WHO, 2012). Daily sodium intake mainly came from one plate meals in the campus cafeteria (Salaya campus, Mahidol University) which the average was 2.85 g of sodium/day in males and 2.04 g of sodium/day in females (Pavadhgul *et al.*, 2009). A study conducted among 320 hypertensive patients in hypertension (HT) clinic at Siriraj Hospital. The mean total daily sodium intake was found to be 3.4 g of sodium/day (Buranakitjaroen *et al.*, 2013). This study could be provided an overview of sodium content in sport drink samples.

Interestingly, a new technique called digital image-based colorimetry (DIC) based on measurement of the red, green and blue (RGB) value of different color intensities will be used instead of spectrophotometry. Modern satellite image interpretation also use bands and spectrum from pixels array as a tool to analyze specific matrix on earth. The method is also called remote sensing photogrammetry (Xu *et al.*, 2012). The RGB value provided the integer scale in ranges from 0 to 255 for each color giving more than 16 million different colors (from 0 to $255 \times 255 \times 255 = 16,777,216$). This technique can be used for reading a RGB or pixels array value of each color from the colorimetric reaction directly and/or recorded digital image which was read the pixels array value by color-analysis software (Lopez-Molinero *et al.*, 2010). The previously studies were used photogrammetric method include the prediction of iron (Suzuki *et al.*, 2006) and calcium in water (Lopez-Molinero, *et al.*, 2013). In addition, the novel method can be improved for determination of sodium which was based on the specific

flame color coupled with pixels array reader program. Several methods have been reported previously for the determination of sodium ion including ion chromatography (Caland *et al.*, 2012), flow injection analysis (Abramova *et al.*, 2009), capillary electrophoresis (Kubán *et al.*, 2014), chromatographic (Svensson *et al.*, 2005) and spectrophotometric method (Taylor *et al.*, 2006). However, a report of photogrammetric method for the determination of sodium in sport drink samples based on pixels array value from digital image of flame emission has not been yet available in the literatures.

The main purpose of this work is to study the possibility of using digital images from camera and read pixels array value by pixels reader program (GetPixel Version 1.0) for determination of sodium in sport drink samples. The proposed method is based on aspirated the standard or sample solution into the burner which ignites the flame by mixing fuel between air and acetylene. Digital images of flame emission were recorded using digital camera. The images of the flame from standard sodium solution and sport drink samples were processed to read the pixels array value using in-house GetPixel program. The arrays of pixels were then normalized using mathematical deconvolution to achieve delegate data represent concentration scale of each standard. The delegate data were then plotted against concentration to obtained calibration curve where the suspected samples were correlated to predict its unknown concentration.

Materials and methods

Chemicals

1. Sodium chloride, Analytical grade, Sigma-Aldrich; Germany
2. Potassium chloride, Analytical grade, Ajex Finechem; Australia
3. Zinc chloride, Analytical grade, Ajex Finechem; Australia
4. Magnesium chloride hexahydrate, Analytical grade, BDH, UK

Instrumentations

1. Android smartphone
2. Mirrorless digital camera A and B
3. Flame atomic absorption/emission spectrophotometer, PinAAcle 900F, PerkinElmer®; USA
4. Deionized water unit, Millipore® Milli-Q; USA

Procedure

Standard of sodium solution preparation

Standard stock solution was prepared by accurately weighing 2.5421 g of sodium chloride into 1 L volumetric flask and adjusting to volume with deionized water to provide a final concentration of 1000 $\mu\text{g mL}^{-1}$. Sodium standard solution in concentrations of 0.4, 0.8, 1.2, 1.6 and 2.0 $\mu\text{g mL}^{-1}$ were prepared by pipet 1 mL of 1000 $\mu\text{g mL}^{-1}$ sodium standard solution and made up the solution to 100 mL with deionized water. Afterward, to pipet this sodium standard solution for 2, 4, 6, 8 and 10 mL and made up the solution to 50 mL with deionized water which were gave the appropriated standard sodium solution.

Calibration curve

The working solution of sodium standard for photogrammetric method with concentrations ranging from 0.4–2.0 $\mu\text{g mL}^{-1}$ were prepared and investigated. Each of sodium standard solution was aspirated into a titanium burner head with 100 mm in length of single slot which was ignited the flame by mixing fuel between air and acetylene. The flame emission digital image of each sodium standard solution was taken by android smartphone, mirrorless digital camera A and B and stored a picture as jpeg format. The digital image of flame emission was processed RGB pixels array values using in-house pixels reader program (GetPixel Version 1.0). The pixels array were then calculated by mathematical deconvolution of golden-yellowish flame. This blue background in pixels were subtracted using $(R-B) \times (G-B)$ photogrammetric deconvolution in each cell of matrix. All cells were averaged to delegate one significant value represent sodium signal per concentration. After that, plot the delegated deconvolution values against concentration to obtain calibration curve where sample pixels were correlated to find out its unknown concentration or amount.

Sample measuring

The commercial sports drink samples were collected from convenient store at Khon Kaen University, Thailand and Vientiane capital, Lao PDR. All of sample were diluted with deionized water in order to get the appropriate concentration for direct determination (Hwang *et al.*, 2017). The diluted sample was flow through flame burner with appropriate flow rate which was recorded the digital image of flame emission as jpeg format, then pixels array value was proceeded by GetPixel program.

RGB-Photogrammetry program

The image of flame emission was interpreted by a pixels array reader program (GetPixel Version 1.0) which was provided by Assist. Prof. Dr. Senee Kruanetr, Department of Chemistry, Faculty of Sciences, Mahasarakham University, Thailand. The Getpixel program was developed in-house using Microsoft Visual Basic 6.0.

Results

Validation of the method

The studies investigated the optimum conditions for sodium determination. Flame emission was carried out with titanium burner head with 100 mm in length of single slot which were applied with air and acetylene. The optimization of experimental conditions were conducted by mean of univariate method, in which one variable was modified while maintaining other variables at constant (Table 1).

Effect of oxidant and fuel flow rate

This study was investigated for flame emission properties. The optimum condition could be provided a flame color to be bright of golden-yellowish and gave a stable flame emission intensity. The source of flame came from the mixing fuel between air (oxidant) and acetylene (fuel). The Syngistix® for AAS software (PerkinElmer®) was used for controlling air and acetylene flow rate. The optimum air flow rate was studied in the range of 6.0–14.0 L min^{-1} . It was found that 10.0 L min^{-1} of air flow rate was gave the suitable flame.

The effect of varying flow rate of acetylene between 1.0 and 3.0 L min^{-1} was examined. The optimum intense flame color was observed when flow rate of acetylene was

2.5 L min⁻¹. The appropriate of air and acetylene flow rate for the experiment were 10.0 and 2.5 L min⁻¹, respectively.

Effect of standard or sample flow rate

The influence of the standard or sample flow rate was investigated by aspirating volume of 4.0, 5.0, 6.0, 7.0

and 8.0 mL min⁻¹ into the flame on burner head with 100 mm in length of single slot. It was found that the 6.0 mL min⁻¹ of standard or sample flow rate which exhibited the greatest intense flame color and chosen as optimum standard or sample flow rate.

Table 1. The optimum conditions for flame emission intensity.

| Conditions studied | Range studied | Optimum level |
|--|----------------------------|---------------|
| 1. Flow rate of oxidant (Air), L min ⁻¹ | 6.0, 8.0, 10.0, 12.0, 14.0 | 10.0 |
| 2. Flow rate of fuel (Acetylene), L min ⁻¹ | 1.0, 1.5, 2.0, 2.5, 3.0 | 2.5 |
| 3. Flow rate of standard or sample aspiration rate, mL min ⁻¹ | 4.0, 5.0, 6.0, 7.0, 8.0 | 6.0 |

Effect type of digital cameras

Sodium standard solution 2.0 µg mL⁻¹ was flowed through the flame on burner head as a representative signal. The digital image of flame emission was then taken and stored as jpeg format with digital camera from android smartphone, mirrorless digital camera A and B (Figure 1) as the conditions shown on Table 2. The compressed file at 880 x 850 pixels size were cropped by the user and read pixels array values by in-house color-analysis software (GetPixel Version 1.0). It were seen that digital image of flame with true color (golden-yellowish) could be obtained when using mirrorless digital camera B for recording flame image (Figure 1(c)). Therefore, the mirrorless digital camera

B was chosen as the selected digital camera instead of android smartphone and mirrorless digital camera A which was applied to the next study.

Regions for reading pixels array values

The proposed method reads pixels array values by color-analysis software (GetPixel Version 1.0). The region was assigned, (Figure 2), for recorded pixels array values of each flame emission image. The average values of pixels array were mathematical deconvoluted and averaged which was used for speculate unknown sodium concentration from samples. The analytical characteristic for determination of sodium in sport drinks will be proceed in the next step.

Table 2. The studies on type of digital camera for stored the flame digital image.

| Type of digital camera | Conditions for stored image | Quality of image (megapixels) |
|--------------------------------|---|----------------------------------|
| 1. Android smartphone | S = 1/33, f = 2.2, ISO 1250 Fix lens 4 mm, Mode: Automatic | 13.0 (jpeg) |
| 2. Mirrorless digital camera A | S = 1/30, f 5.0, ISO 1600 Zoom lens 18-55 (at 50mm) Mode: Automatic | 18.0 (jpeg) |
| 3. Mirrorless digital camera B | S = 1/30, f = 5.6, ISO 1600 Zoom lens 16-50 (at 50mm) Mode: Manual | 16.1 (jpeg) |

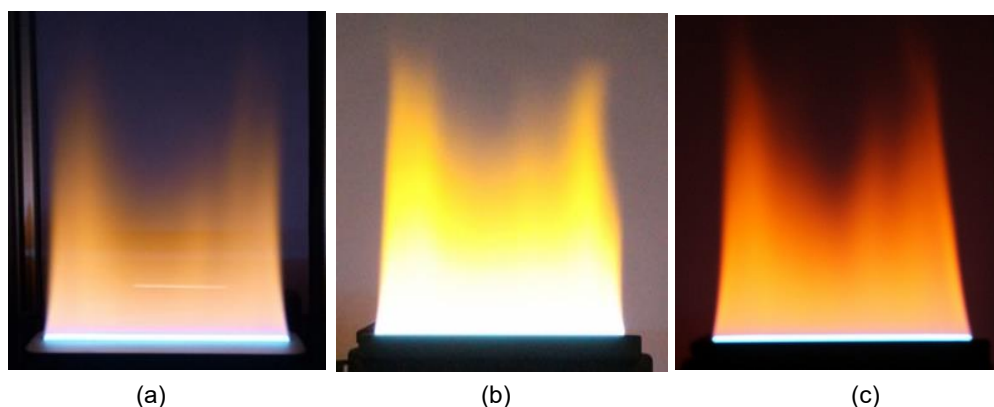


Figure 1. The $2.0 \mu\text{g mL}^{-1}$ sodium standard solution was used for taking a flame image with (a) android smartphone; (b) mirrorless digital camera A; (c) mirrorless digital camera B

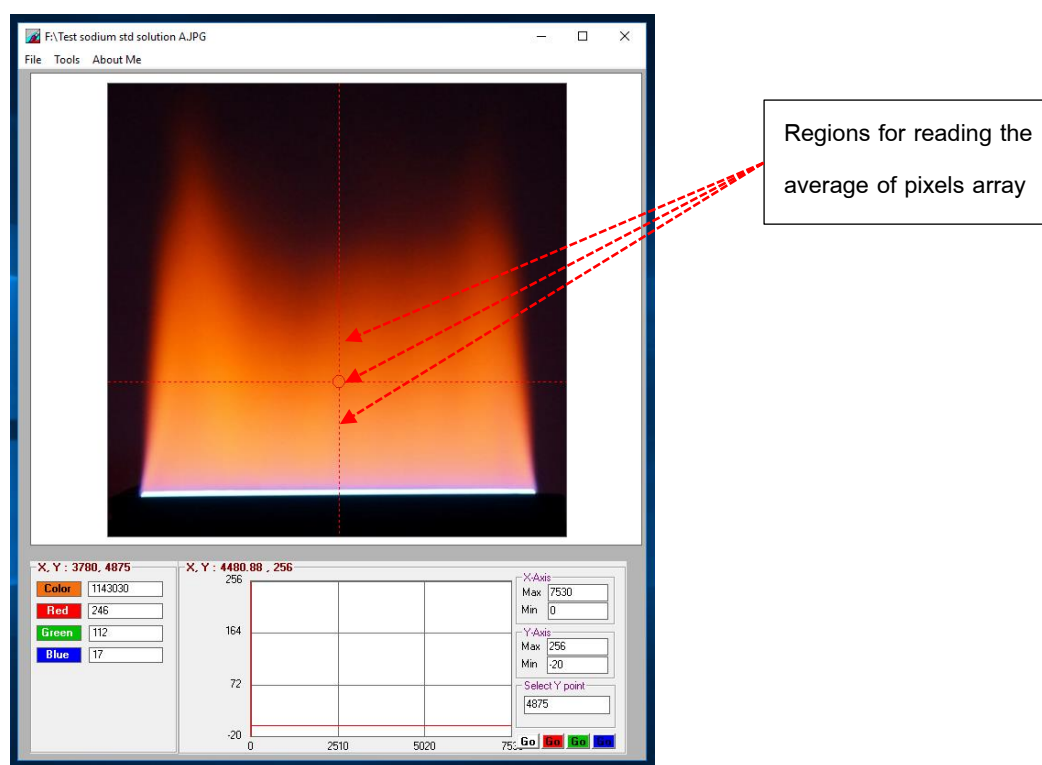


Figure 2. GetPixel program was used for color-analysis.

Analytical characteristics

Using the proposed procedure for determination of sodium in sport drinks under the optimum conditions. Analytical characteristics of the method were shown in Table 3. The calibration curve for standard sodium solutions shown an excellent linearity over a concentrations range of $0.4\text{--}2.0 \mu\text{g mL}^{-1}$. Over the above concentrations range, linear regression of the average deconvoluted pixels array values (y) and concentration of sodium (x) expressed the

equation $y = 2.9031x + 0.9313$. The correlation coefficients was shown to be 0.9901 ($n=5$). Some of flame images (blank and standard sodium solution) were shown in Figure 3. The limit of detection (LOD) and the limit of quantitation (LOQ) were determined. For sodium, based on the criteria of signal-to-noise ratio are 3:1 and 10:1, respectively. The results of LOD and LOQ were found to be 0.12 and $0.38 \mu\text{g mL}^{-1}$, respectively.

The precision study (standard deviation) was obtained after seven replicated assays of low and high concentration of sodium standard (0.8 and $1.6 \mu\text{g mL}^{-1}$) were measured. The relative standard deviation value of low and high concentration of assays were 0.23 and 0.24 %. The accuracy of the method is expressed in terms of percentage recovery of sodium in standard solution (0.6 and $1.8 \mu\text{g mL}^{-1}$, $n=7$). The percentage recoveries were found to be 103.03 and 102.77 %, respectively.

The proposed method was applied to quantification sodium from sport drink samples and the results were

compared to the reference method (performed by flame atomic emission spectrophotometry, FAES). FAES was operated with an air-acetylene and the flow rates were 10 L min^{-1} of air and 2.5 L min^{-1} of acetylene. Emission intensity signal were measured using 589.0 nm line at a bandpass of 0.2 nm (Hwang *et al.*, 2017). The accuracy was verified by the Student's *t*-test. The calculated Student's *t*-test value (0.30) was less than the theoretical (2.45) at a confidence level 95% (*P* value of 0.05). Reasonable agreement between the proposed method and FAES methods was found (Table 4).

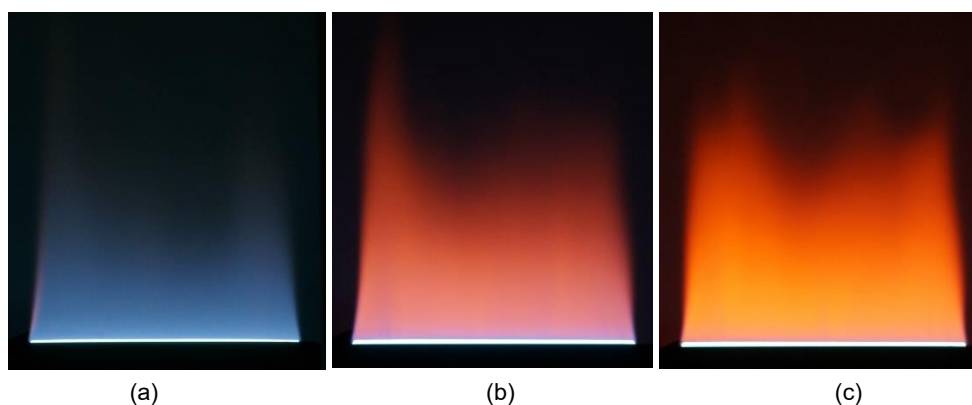


Figure 3. Examples of flame digital image of, (a) Blank solution; (b) $0.4 \mu\text{g mL}^{-1}$ sodium standard; (c) $1.6 \mu\text{g mL}^{-1}$ sodium standard

Table 3. Analytical characteristics of proposed method for determination of sodium.

| Parameters | Optimum value |
|--------------------------------------|---------------------------------|
| Linearity of calibration curve | $0.4 - 2.0 \mu\text{g mL}^{-1}$ |
| Linear regression equation ($n=5$) | $Y = 2.9031X + 0.9313$ |
| Correlation coefficient | 0.9901 |
| Limit of detection, LOD | $0.12 \mu\text{g mL}^{-1}$ |
| Limit of quantitation, LOQ | $0.38 \mu\text{g mL}^{-1}$ |
| Repeatability ($n=7$); RSD | |
| $0.80 \mu\text{g mL}^{-1}$ | 0.23 % |
| $1.60 \mu\text{g mL}^{-1}$ | 0.24 % |
| Percentage recoveries ($n=7$) | |
| $0.60 \mu\text{g mL}^{-1}$ | 103.03 % |
| $1.80 \mu\text{g mL}^{-1}$ | 102.77 % |

Some of flavor sugars used in the manufacturing of sport drinks such as glucose, dextrose and sucrose could interfere with photogrammetric method and the quality of results. Similarly, some metal ions contained in sport drink samples namely potassium(K^+), magnesium(Mg^{2+}) and zinc(Zn^{2+}) may also interfere in the proposed procedure. These potential interfering substances were then added

one-by-one to the tested samples at concentration ranges 10 and 25-fold higher than the concentration of sodium solution ($2.0 \mu g mL^{-1}$). It was found that all of flavor sugars and metal ions were interfered the monitoring signal less than $\pm 2.5 \%$ for determining the sodium solution.

Table 4. Accuracy of proposed method compared with flame atomic emission spectrophotometric method (FAES) for determination of sodium in sport drink samples.

| Sport drinks sample | Sodium found, $n=5$ | |
|---|---|---|
| | Proposed method ($\mu g mL^{-1} \pm SD$) | FAES method ($\mu g mL^{-1} \pm SD$) |
| SD 01 | 737 ± 3.29 | 744 ± 2.17 |
| SD 02 | 344 ± 3.68 | 327 ± 3.49 |
| SD 03 | 955 ± 3.88 | 938 ± 2.80 |
| SD 04 | 452 ± 2.95 | 439 ± 3.16 |
| SD 05 | 325 ± 2.10 | 305 ± 2.30 |
| SD 06 | 842 ± 2.54 | 867 ± 1.80 |
| SD 07 | 388 ± 2.22 | 408 ± 2.15 |
| <i>t</i> -test at 95% confidence level: | | |
| <i>t</i> -calculation | | 0.30 |
| <i>t</i> -distribution at $(n-1)=6$, | | 2.45 |

Discussion and Conclusions

A photogrammetric method for determination of sodium in sport drinks was developed. The proposed method was based on aspirated sodium solution into burner which was operated with an air-acetylene flame. The flame image was taking by mirrorless digital camera and stored as jpeg format. The digital image of flame emission was processed RGB pixels array values using in-house pixels reader program (GetPixel Version 1.0). The pixels arrays were then calculated by mathematical deconvolution of golden-yellowish flame. Afterward, plot the delegated deconvolution values against concentration to obtain calibration curve where sample pixels were correlated to find out its unknown concentration of sodium in sport drink samples. The linearity of the calibration curve is in the useful range for determination of sodium in sport drink samples.

The proposed simple photogrammetric method and reference FAES method showed positive agreement with no statistical difference at 95% confidence level by the *t*-test. The study in this work has demonstrated the potential for photogrammetric technique.

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