Method of vis spectrometry based on measuring solution color, using digital camera and digital image processing

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ABSTRACT

Method of molecular absorption spectral analysis in visible region is developed where the solution color is measured instead of determining the absorbance of the solution. Solution color is measured by a digital camera. To define the solution color, CIE RGB colorimetric system is used. A dependence of any of the three (R, G or B) tristimulus values on concentration is applied for finding analyte concentration. Intensity of the light source, respectively, intensity of the light passed through the test solution, affects the sensitivity of analysis, as well as the range of concentrations to be determined by this method. Solutions of $K_2Cr_2O_7$, $KMnO_4$, $Fe^{3+}$, $Cu^{2+}$, and $NH_4^+$ are analyzed. The analysis can be done with any spectrophotometer, if it is possible a digital camera to be put in the path of the light beam after the cuvette. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Vis Spectrophotometry:
Dependence of solution color on concentration;
Use of a digital camera for determining solution color.

INTRODUCTION

Spectrophotometry is one of the oldest analytical methods, known since 19th century, which even to this day is among the most used method for chemical analysis of low concentrations of elements. During the all period of time of its existence, spectrophotometry has undergone great development. A variety of methods have been developed, but the relationship between absorbance and concentration, that all these methods are base, has been remained unchanged. In a Patent[1] another approach is suggested: to make molecular absorption analysis in the visible spectrum without measuring the absorbance. The proposed here method is similar to the spectrometry because it utilizes spectrometric apparatus, and monochromatic light is passed through the test solution. Unlike the ordinary method, for which intensity of light is measured, absorbance is calculated and concentration is determined by the absorbance, for the proposed method, solution color is measured and by means of it the concentration is determined. Relationship between solution color and concentration is well known: a paler color of the solution complies with a lower concentration and hence darker color means higher concentration of the solution.

Very common scheme for measuring the color is the additive one. The most popular additive system, created even as early as in 1931 by the International Commission on Illumination (CIE), is CIE RGB color system[2]. According to it, any color can be prepared by mixing different amounts of the three primary colors, called tristimulus. These are the colors red (R), green (G) and blue (B). A color is determined if values of R, G and B are known. Tristimulus values of each of
the three colors vary in the range from 0 to 255. The determination of color is performed using an apparatus called tristimulus colorimeter. In the literature\cite{3} it is shown that the digital camera can serve as a tristimulus colorimeter. In this work the method described in the Patent\cite{1} is realized as digital camera is used for determining the color of the solution.

**EXPERIMENTAL**

**Reagents and solutions**

All reagents in the analyses are of analytical purity classification. Doubly distilled water is used. Procedures for preparation of color solutions, used for analysis, are the same as these for standard spectrophotometric analysis.

**Apparatus**

Use is made of a spectrophotometer Specol-10 (Germany) with a spectrophotometric titration device. It has a cuvette with volume of 30 cm$^3$ and an optical path of light through a solution of 2 cm. Photo cell of the titration device is replaced by a digital camera. An amateur digital camera Panasonic Lumix, Model No DMC-LS5, 14 mega pixels, is used.

**Procedure for analyses**

Standard and analyzed solutions are placed consecutively in the cuvette and a picture of each solution is taken. The accumulated digital information in the camera is then transferred to a PC via a cable or a capture card of the camera. Tristimulus values of the solution images are determined. Dependences of each tristimulus values on concentration are found and the most appropriate of them is selected. An equation is used to describe mathematical relationship between a tristimulus value and concentration of the standard solutions. This equation is then used to calculate the unknown concentration.

**Software**

Software is created by one of the authors of the article, specifically for the purpose of the analysis. It includes: removing the background from an solution image, determining the tristimulus values of the standard and analyzed solution images, finding the dependencies of tristimulus values of R, G and B on concentration of the standard solutions, testing various algorithms that describe the dependence of selected tristimulus value on concentration of the standard solutions, showing these relationships graphically and calculating the concentration of the unknown solutions.

**RESULTS AND DISCUSSION**

A digital image of a color solution that is captured, using the apparatus described above, represents a colored stripe, positioned vertically in the center of the frame, surrounded by a dark (black) background. Two methods are tested to separate a color sample from the picture. One way is to select a rectangular section from the color stripe by mouse clicking. Another way tested is by software. For yellow colored solution of K$_2$Cr$_2$O$_7$, which concentration is 75 µg/cm$^3$, for five parallel determinations carried out by a mouse clicking selection, results obtained are: $\bar{x} = 74.8$ µg/cm$^3$, SD = 0.81 µg/cm$^3$, and by software selecting respectively: $\bar{x} = 74.8$ µg/cm$^3$ and SD = 1.46 µg/cm$^3$. In this experiment the software method of selecting is less reproducible, but in general this method gives more accurate information on the image, because the entire image is interpreted, while with the mouse clicking selection only a part of the color stripe is treated. A selection with mouse clicking can be an advantage if the color stripe is inhomogeneous, because a selection can be made from a homogeneous part of the stripe. Therefore, both methods can be used, but the software one is necessary to be improved.

A digital image of the solution is derived from millions of color dots, each of which is determined by three (R, G and B) tristimulus values. An analogy can be made with color and wavelength of light and color and tristimulus values. Every three tristimulus values correspond to a specific wavelength. It follows that individual color dots composing the image have different colors and therefore different values of R, G and B. Figure 1 shows a statistical distribution of R, G and B tristimulus values of an image of a yellow colored solution of K$_2$Cr$_2$O$_7$, having 80 µg/cm$^3$ Cr (VI).

Since every single color is represented by one value of R, one value of G and one value of B, but there are different values for R, G and a B, it is reasonable to choose the most frequently appeared values of R, G
and B, that corresponds to a predominant color of the solution image. For distribution curves of R and G, having well-defined peaks, the dominant values of R and G are these corresponding to the maximums of respective curves. The curve of B differs from the other two curves. It has not a peak, but a plateau. In this case it is suitable to take an average of all available values of B. The appropriateness of this approach was experimentally confirmed. From the other side ascending and descending branches of the distribution curves of R and G are almost symmetrical to the respective maximums of the curves, and for the symmetrical curve a tristimulus value corresponding to the peak of the curve coincides with the average value obtained from all available values. Thus averaging of the tristimulus values seems to be a right way for finding tristimulus values of an image.

In view of the fact that final goal of the work is solution concentration to be determined, and as the solution color is defined by R, G and B tristimulus values, it is necessary to find a dependence of all three (R, G and B) tristimulus values on concentration. In the present work this task is solved by a linear regression analysis.

Figure 2 shows the dependence of each of the three tristimulus values on concentration of the same solution of \( \text{K}_2\text{Cr}_2\text{O}_7 \). It is noteworthy that all three tristimulus values vary with the concentration changes, but while tristimulus values of R and G vary slightly, the tristimulus value of B amends significantly. The same is seen for the other examples of analysis developed in the work: one of the three tristimulus values undergoes significant changes with changes in concentration, while for the other two tristimulus values the changes are weaker. It is obvious that for finding the concentration it is sufficient to know only one of the three dependencies of tristimulus values on concentration. From the viewpoint of the sensitivity of analysis, it is more appropriate to work with this tristimulus value, for which the changes are great, instead using any of the other two tristimulus values. For the same example of analysis: \( \text{K}_2\text{Cr}_2\text{O}_7 \) solution, concentration of 75 \( \mu \text{g/cm}^3 \), mouse clicking selection, when using B tristimulus value, results are as follow: \( \bar{x} = 74.8 \mu \text{g/cm}^3 \), SD = 0.81 \( \mu \text{g/cm}^3 \). When using all three tristimulus values and linear regression analysis, the results are respectively: \( \bar{x} = 75.0 \mu \text{g/cm}^3 \), SD = 1.15 \( \mu \text{g/cm}^3 \). Therefore analysis is not only simpler, but more reproducible, when using the most changing tristimulus value.

It can be seen from curve B, Figure 2, tristimulus value of B at low concentrations has a slight slope. At higher concentrations, the curve has a steep slope and after that the curve slope is again slight. It is appropriate to use the middle part of the curve where the slope is steep, the analysis is sensitive and analytical results are better than when using the two curves parts having slight slopes. A standard calibration curve, such as that of curve B, Figure 2, is described by a polynomial regression of first to fourth order. The order of the polynomial regression depends on a section of the steep part of the curve which is treated.

Figure 3 shows an influence of light source intensity, respectively of an intensity of the light, passing through the test solution, on an appearance of a graph, illustrating a dependence of tristimulus values on solu-
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Different color solutions were analyzed in the work, by the method proposed. The analysis was conducted with two light sources, with different intensity, that are identical to those used in the experimental work, data of which are shown in Figure 3. With every one of the two light sources were analyzed two solutions with different concentrations. Five examples of analysis were tested. Each example was analyzed four times (each time with different concentration). Data from the analyses are presented in TABLE 1. The results obtained from these analyses are not as good as those from the spectrophotometric analysis, but a knowledge acquired when we was developing the method, gave us an idea of possible ways to improve the results of the analysis, in our future work.

Some statements derived from the created work as follows:

Proposed method is simpler for implementation than the spectrophotometry because it needs only one measurement (that of solution color) and it is not needed reference solution, against two measurements of light intensity for the spectrophotometric method.

A digital camera does not only serve as a light detector, but data acquired have direct correlation with the solution concentration, while for spectrophotometry a detector signal has to be first multiplied, then to be transform into a function (absorbance), having a relation to concentration.

An inclusion of a digital camera into a spectrophotometer actually creates a new separate line of analysis. In this way the proposed method become an alterna-

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**Figure 3:** Influence of the light source intensity to the graph curve of tristimulus value against solution concentration. 3.1- for tristimulus value of B, 3.2- for tristimulus value of R and 3.3- for tristimulus value of G. I-for less intense light source and II-for more intense light source.
An image capturing with a digital camera is a highly automated process that contributes analysis process to be easy automated.

A digital camera is adapted for direct connection to a computer; the digital information from the camera can be immediately processed for analysis and advantages of all possibilities offered by the computer to be taken.

Nevertheless a digital camera has many functions, it is compact, and its size is relatively small, which allows minimizing dimensions of a spectrophotometer with a digital camera.

A digital camera, in certain conditions, can serve as an absolute tristimulus colorimeter, so it is possible an absolute analysis to be performed, i.e. an analysis without using standard or etalon solutions, but only by experimental data, established in advance, for an color and corresponding to it concentration of the solution.

The presented method is based on the use of only RGB colorimetric system. There are many other colorimetric systems, which is a prerequisite for further de-

<table>
<thead>
<tr>
<th>Species to be determined</th>
<th>Colored species</th>
<th>Introduce, µg/cm³</th>
<th>Found* ( x \pm ts \sqrt{n} ) µg/cm³</th>
<th>Relative standard deviation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>( \text{K}_2\text{Cr}_2\text{O}_7 )</td>
<td>32</td>
<td>31.0 ± 0.5</td>
<td>1.9</td>
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<td></td>
<td></td>
<td>36</td>
<td>35.8 ± 0.9</td>
<td>2.8</td>
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<td>75</td>
<td>74.8 ± 0.7</td>
<td>1.1</td>
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<td></td>
<td></td>
<td>85</td>
<td>85.2 ± 0.3</td>
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<tr>
<td>Mn</td>
<td>( \text{KMnO}_4 )</td>
<td>11</td>
<td>10.8 ± 0.1</td>
<td>0.8</td>
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<td></td>
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<td></td>
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<td>23</td>
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<tr>
<td>Fe</td>
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<td></td>
<td>3</td>
<td>3.3 ± 0.1</td>
<td>4.9</td>
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<td>4</td>
<td>4.1 ± 0.0</td>
<td>0.8</td>
</tr>
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<td>5</td>
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<td></td>
<td>100</td>
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<td>4</td>
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<td>4.7</td>
</tr>
</tbody>
</table>

\* \( t \) is Students t-value at 95% probability, \( s \) is standard deviation, \( n \) is number of determination, \( n = 5 \).
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velopment of the method.

REFERENCES


