



Determination of magnesium by the solution scanometric method in a coloured titan yellow magnesium hydroxide complex form

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Received 16 April 2015; received in revised form 4 August 2015; accepted 5 August 2015

Available online 10 November 2015

Abstract

In this work, the magnesium content was determined by the solution scanometric method using titan yellow (TY) as a complexing agent in alkaline media. This method is based on scanning a solution containing the pink-coloured product of the combination of TY and the magnesium hydroxide complex. Hydroxylamine hydrochloride (HA) and starch were utilised as colour stabilizers and protective colloids, respectively. After the cells containing the sample solution were scanned, the colour of each cell was analysed with software written in Visual Basic (VB 6) in terms of the red, green and blue values. The parameters used for optimisation include the reaction time and the concentration of TY, sodium hydroxide, starch and HA. The system had a wide linear range between 0.070 and 30.000 $\mu\text{g mL}^{-1}$ concentrations of magnesium, with a detection limit of 0.058 $\mu\text{g mL}^{-1}$ and a relative standard deviation of 1.90% for the G colour value. In addition, the effects of some foreign species were investigated. The method was successfully applied for the determination of magnesium in almond gum and three water samples.

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Keywords: Magnesium; Solution scanometry; Titan yellow; Plexiglas® cell

1. Introduction

Magnesium is the eighth most abundant element in the crust of the Earth. The determination of alkaline earth metals, particularly magnesium, is of importance for environmental, biological and industrial applications [1]. Magnesium, an abundant mineral in the body, is

naturally present in numerous foods, added to other food products, available as a dietary supplement, and present in some medicines (such as antiacids and laxatives). It is also a cofactor in more than 300 enzyme systems that regulate diverse biochemical reactions in the body [2–4].

Several reagents for the determination of magnesium have been described in the literature, such as eriochrome black T [5], titan yellow (TY) [6,7], ammonium phosphate method [8], EDTA [9], paratolyl-2-thenohydroxamic acid and quinalizarin [10], 4 methyl-3-((1-H-Indol-3-yl) (phenyl) methyl)-1-H-Indol (MPBIM) [11] and trizma-chloranilate [12].

TY, also known as thiazole yellow, titangelb, clayton yellow and direct yellow 9, is a triazene dye that is used in display devices [13], optical sensors [14], lithographic processes [15], inks [16], paints [17], and incandescent

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Peer review under responsibility of Taibah University.



electric lamps [18] as well as an albumin detector [19], fluorescent indicator in microscopy, and acid–base indicator [20]. It is also used as an important reagent for the detection of magnesium [7,21].

With the large contribution of Kolthoff [21] in 1926, TY was introduced in 1926 as an outstanding reagent for the determination of Mg^{2+} ions, after which the detection method was further developed through the co-operation of Lehr and Wesemeale (1950) [7]. Among all of the techniques for this determination, the procedure of Neil [6] in 1965 was of great importance and was preferred to other methods because it provides a higher ratio of colour intensity/blank.

The solution scanometric technique was introduced recently by Abbaspour et al. [22]. They used commercially available flatbed-scanners to obtain images of coloured solutions. The obtained images were transferred to a computer for an analysis and measurement of the intensity of the solution colour. The method is based on the reaction in solution phase in Plexiglas® cells. The solution was scanned, and the red, green and blue (RGB) colour model was used to analyse the solution color [23–25]. Afterwards, this method was coupled with cloud point extraction as a detection system in our group [26].

Scanometry has several advantages, such as simplicity (handheld scanner and PC), high scanning speed, inexpensive, portability, easy immobilisation of reactants, lack of a requirement of identifying λ_{max} , large archive of experiences, short response time, limited interference, ability to run various tests simultaneously and ability to investigate non-transparent samples by analysing the reflective properties of the surface.

In the present work, solution scanometry, as a simple, fast, and costs effective method, was developed to determine the Mg^{2+} ion content based on the formation of a pink coloured complex between Mg^{2+} ions and TY in sodium hydroxide medium and in the presence of starch as a colloidal protector and in the presence of HA as a colour stabilizer.

2. Experimental

2.1. Apparatus

The cells (with 1000 μL volume each) were built by using a sheet of Plexiglas® [22]. A Canoscan LiDE 200 flatbed scanner was used to scan the Plexiglas® sheet. The horizontal and vertical resolution of the scanner was set to 300 dpi. Furthermore, the colour of each cell was analysed with respect to the red, green and blue values using software written in Visual Basic 6 (VB 6) for

[27,28]. Three Biohit proline pipettors with different volumes between 0.5 and 1000 μL were used for injecting samples into the cells.

2.2. Chemicals and reagents

All of the chemicals used in this work were of analytical grade. In addition, double distilled water was used throughout. TY was purchased from Merck (E. Merck, Darmstadt, Germany). A laboratory stock solution (0.02%, w/v) was prepared by dissolving crystalline TY in double distilled water. The analytical-grade magnesium nitrate, sodium hydroxide, starch and hydroxylamine hydrochloride used in this study were obtained from Merck.

2.3. Principles of the red, green and blue (RGB) colour systems

The RGB colour system works on the basic principle that any colour is composed of red, green and blue. Colours are created by adding more light to a starting colour of black, and for this reason, it is also known as the additive colour system. Every colour in the RGB spectrum is made up of a different value for each of its red, green and blue components. Hence, it is used by systems that have the ability to add light, such as LCD, CRT and RGB projectors. RGB colours vary between 0 and 255, a range that a single 8-bit byte can offer by encoding 256 distinct values. In the RGB system, any colour is represented in the form of (R, G, B), in which the (0, 0, 0) and (255, 255, 255) refer to black and white, respectively. Therefore, by increasing the intensity of colours, the colour values are decreased. In this system 16,777,216 colours can be made. Any colour can be described by the following formula:

$$V = R + 256G + 256^2B$$

where R, G and B are red, green and blue values of the main colour, respectively. For black and white, V is equal to 0 and 16,777,216, respectively. By using the following flowchart, R, G and B values of V for any colour can be extracted:

$$R = V \bmod 256$$

$$G = \frac{(V - R) \bmod (256^2)}{256}$$

$$B = \frac{V - R - G \times 256}{256^2}$$

“Mod” is a numeric function which returns the remainder when dividing two numbers.

It should be mentioned that having only one of the R, G and B colour values that have the same colour as the solution is usually useless because this value is often greater than 200 and does not significantly change during the experiment. In this experiment, the effective intensity of all three parameters of the RGB changed; therefore, the one with the largest change, i.e., the “G” parameter, was chosen.

2.4. Procedure

Forty-five microlitres of 5% (w/v) HA, 25 µL of a 1% (w/v) of starch stock solution, 175 µL of a 0.02% (w/v) TY solution, 50 µL of 100 µg mL⁻¹ magnesium nitrate and 55 µL of a 6 mol L⁻¹ sodium hydroxide solution were transferred into each cell and an appropriate volume of deionised water added to bring the total volume in each cell to 500 µL. The cells were shaken to obtain a homogenous colour; after 5 min, the Plexiglas® sheet was scanned with the scanner, the image was transferred into the computer, and any colour changes in the cell related to the blank (a sample solution without Mg²⁺ ions) were analysed using a program written in VB 6. In this program, the colour of each cell is analysed based on the RGB system in terms of the R, G and B values. It should be noted that in the colour analysis programs, a specific area of approximately 10,000–300,000 was selected for analysis and the R, B and B values were averaged over pixels in this area. In this way the noise can be dramatically reduced. The effective intensity of colour values was calculated as follows:

$$A_r = -\log \left(\frac{R_s}{R_b} \right)$$

$$A_g = -\log \left(\frac{G_s}{G_b} \right)$$

$$A_b = -\log \left(\frac{B_s}{B_b} \right)$$

where A_r, A_g and A_b are the effective intensity for red, green and blue, respectively. R_s, G_s, B_s and R_b, G_b and B_b are the red, green and blue colour values of a sample and a blank, respectively.

2.5. Preparation of real samples

2.5.1. Water samples

The Mg²⁺ ion was determined using the solution scanometric method in three water samples, including

tap, stream (Yasouj City) and mineral (Sepidan company) water. Forty-five microlitres of each water sample was poured into 50-mL volume flasks and then placed in a water bath at 70 °C for 20 min. Then, the solution became acidic, and sodium tungstate was added to precipitate cations that interfered with Mg²⁺ ion determination. The sample solution was filtered through paper filter. The volume of solution passed reached 50 mL with double distilled water, and 200 µL of the cited solution was used for determination of magnesium by the solution scanometric method.

Additionally, the Mg²⁺ ion content was determined in these samples by the atomic absorption spectroscopy (AAS) method. The conditions for the determination of the Mg²⁺ content by AAS are: wavelength; 285.2 nm, slit; 0.7 nm, flame; and C₂H₂–air; also a magnesium hollow cathode lamp was used.

2.5.2. Almond gum sample

For the determination of the Mg²⁺ ion content according to Section 2.4 by the standard addition method, 0.5 g of almond gum samples were washed with distilled water to remove dirt and impurities and dried at 120 °C for 30 min. For acid treatment, the sample was mixed with concentrated hydrochloric acid (37%) at room temperature for 24 h. The sample was filtered through filter paper and washed several times with double distilled water, after which the obtained product was transferred to a 50-mL volume flask, diluted to the mark with double distilled water, and stored in a closed container for further tests.

3. Results and discussion

This method is based on the combination of TY and magnesium hydroxide to produce a pink-coloured complex that is then scanned. Starch as a colloidal protector and HA as colour stabilizer, respectively, were added to increase the stability of the solution.

3.1. Optimisation the parameters of the system

To optimise this system, the effect of time and the concentration of chemical reagents were investigated.

3.1.1. Effect of time

For the acquisition of the maximum signal, it was required that the interaction between reagents be complete. Reaction times in the range of 1–40 min were studied. For this purpose, the cell containing the 500 µL solution of 0.45% HA, 0.05% starch, 0.007% TY, 10 µg mL⁻¹ magnesium and 0.66 mol L⁻¹ sodium

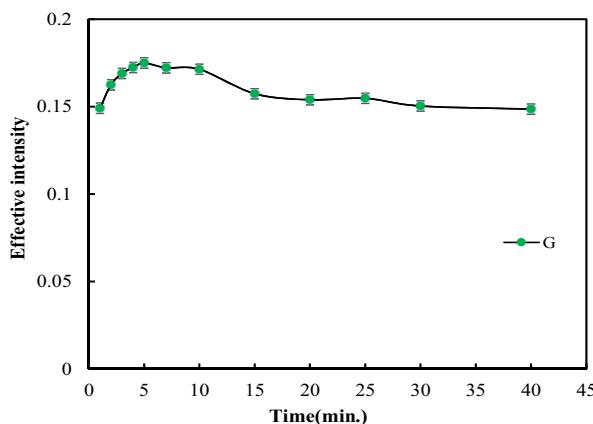


Fig. 1. The effect of time on the effective intensity (conditions: 500 μL of a solution containing $10 \mu\text{g mL}^{-1}$ Mg^{2+} ion, 0.45% (w/v) HA, 0.05% (w/v) starch, 0.007% (w/v) of TY and 0.66 mol L^{-1} sodium hydroxide).

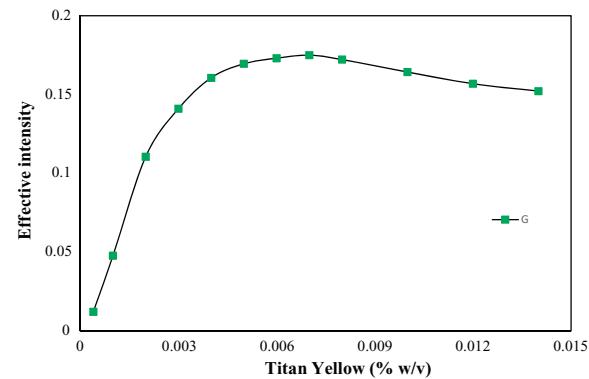


Fig. 2. The effect of the titan yellow concentration on the effective intensity (conditions: 500 μL of a solution containing $10 \mu\text{g mL}^{-1}$ Mg^{2+} ion, 0.45% (w/v) HA, 0.05% (w/v) starch, 0.66 mol L^{-1} sodium hydroxide and different amounts of TY and a reaction time of 5 min).

hydroxide was scanned at 1 or 5 min increments at room temperature, and the image of the cell was analysed using the software. The results are shown in Fig. 1. The best signal was obtained at 5 min. At shorter times, the reaction was not complete, and at longer times, the colour was not stable; therefore, the signal decreased.

3.1.2. Effect of TY, sodium hydroxide, HA and starch concentrations

According to the procedure above, the effect of TY, HA, sodium hydroxide and starch on the effective intensity was investigated. As Fig. 2 shows, the maximum colour intensity was observed at 0.007% (w/v) TY, the concentration at which the interaction between TY and magnesium hydroxide was completed. It is obvious that the formation of the magnesium hydroxide–TY complex is not complete at a low concentration of TY.

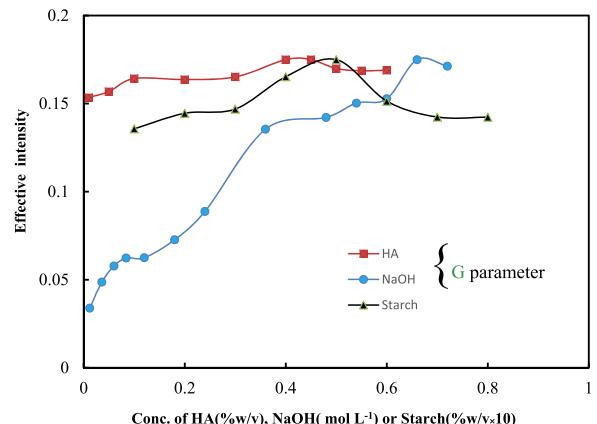


Fig. 3. The effect of the sodium hydroxide, HA and starch concentrations on the effective intensity (conditions: 500 μL of a solution containing $10 \mu\text{g mL}^{-1}$ Mg^{2+} ion, 0.45% (w/v) HA, 0.05% (w/v) starch, 0.007% (w/v) of TY and 0.66 mol L^{-1} sodium hydroxide and a reaction time of 5 min). For two other parameters, the investigated parameter was changed and the others were fixed similarly.

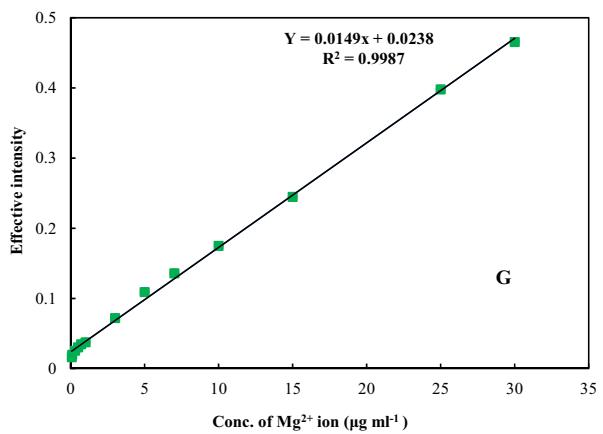


Fig. 4. Calibration curve for the determination of the concentration of Mg^{2+} ions at optimum conditions.

Fig. 3 illustrates the effect of the sodium hydroxide, HA and starch concentrations. It is observed that the effective intensity G increased with the addition of sodium hydroxide. The highest signal was obtained at 0.66 mol L^{-1} of sodium hydroxide. At this concentration, the formation of magnesium hydroxide and following magnesium hydroxide–TY was completed. Thus, as it provided sufficient hydroxide, 0.66 mol L^{-1} was the optimum concentration.

The optimisation of the concentration of starch as a colloidal protector reagent is one of the key optimisation steps. At low starch concentrations (less than 0.01%), the solution sedimented, and at high concentrations, the solution was relatively turbid; therefore, the

Table 1

Effect of interfering species on the determination of $10 \mu\text{g mL}^{-1}$ Mg^{2+} ion at the optimum conditions by solution scanometric method.

Foreign ion	Tolerance conc. ($\mu\text{g mL}^{-1}$)
PO_4^{3-} , SO_4^{2-} , Li^+ , Na^+	5000
Mn^{2+}	1000
Ca^{2+}	100
CO_3^{2-}	50
Zn^{2+} , Co^{2+} , Fe^{3+} , Ni^{2+}	30
Al^{3+}	10

signal decreased. As shown in Fig. 3, 0.045% (w/v) was the optimum concentration.

Of the mentioned interactions, HA is often added to avoid colour fading of a solution [7]. In this way, this stabilizer also prevents oxidation [29]; eliminates

the interference from species, such as manganese and iron [30]; and improves the standard curves [31]. Fig. 3 also illustrates the effect of the HA concentration on the effective intensity of G. As observed, the colour intensity increased with the increasing HA concentration, but decreased after 0.45%. Thus 0.45% was the optimum concentration. It was found that the colour faded rapidly if no stabilizer was added.

3.2. Analytical performance

The calibration curve was plotted under optimum conditions (Fig. 4). A good linear relationship between the effective intensity of the product and the concentration of magnesium was obtained in the range of 0.07 – $30.00 \mu\text{g mL}^{-1}$. The equation for the regression line was $Y = 0.0149 C + 0.0238$ (for G), where C is the

Table 2

Determination of Mg^{2+} ions in water and almond gum samples by the solution scanometric method.

Sample	Regression equation	Found by		Reported by company
		Scanometry	AAS	
		($\mu\text{g mL}^{-1}$)		
Tap Water (Yasouj City)	$0.00131x + 0.04$	10.76	9.65	–
Stream Water (Yasouj City)	$0.0146x + 0.05$	10.17	9.55	–
Mineral Water (Sepidan Company)	$0.0165x + 0.02$	3.63	3.63	4.00
Almond gum	$0.009x + 0.044$	1.36 ^a	1.31 ^a	–

^a For this real sample the unit of concentration is mg g^{-1} .

Table 3

A comparison between the results of solution scanometry and other methods for the determination of the concentration of Mg^{2+} ions by the solution scanometric method.

Method	Analyte(s)	Reagent	Linear range ($\mu\text{g mL}^{-1}$)	LOD ($\mu\text{g mL}^{-1}$)	RSD%	Ref.
Cloud point extraction-flame atomic absorption spectrometry	Mg^{2+} and Ag^+	4 Methyl-3-((1-H-Indol-3-yl)(phenyl)methyl)-1-H-Indol (MPBIM)	0.007–0.200	0.00147	1.17	[11]
Solvent extraction and spectrophotometric determination	Mg^{2+}	Paratoly-2-thenoxyhydroxamic acid and quinalizarin	0.6–10.20	–	3.07	[10]
Cloud point extraction-flame atomic absorption spectrometry	Mg^{2+}	Trizma-chloranilate	5–220	0.75	–	[12]
Derivative spectrophotometry	Ca^{2+} and Mg^{2+}	–	–	0.03	Less than 2%	[33]
<i>Spectrophotometric method</i>						
Sequential injection analysis	Ca^{2+} and Mg^{2+}	<i>o</i> -Cresolphthalein	0–20	0.24	Less than 2%	[34]
Spectrophotometry	Fe, Mn, Ca, Mg, K, Pb, Se	Titan yellow	1.469–4.4450	–	–	[35]
Solution scanometry	Mg^{2+}	Titan yellow	0.07–30.00	0.052	1.90	This work

concentration of Mg^{2+} ions in $\mu\text{g mL}^{-1}$. The detection limit for the G factor, based on three times the standard deviation of the blank ($3S_b$), was found to be $0.05 \mu\text{g mL}^{-1}$ ($n=5$). To ensure the repeatability of the method, 6 sample solutions of $10 \mu\text{g mL}^{-1}$ Mg^{2+} ions were analysed and the Relative Standard Deviation % (RSD) for the G colour values, 1.9%, was obtained. Therefore, the proposed analytical method has good precision, sensitivity and a low detection limit and is suitable for the determination of Mg^{2+} ions in different samples.

3.3. Interference study

The influences of diverse cations and anions on the determination of magnesium were studied. Various amounts of other species were added to a $10 \mu\text{g mL}^{-1}$ solution of magnesium, and the recommended procedure under optimum conditions was applied. An error of less than or equal to $\pm 5.0\%$ in the signal reading was considered to be a tolerable value. The results are shown in Table 1. Interfering elements can be separated by precipitation with sodium tungstate.

3.4. Application

Magnesium, as a physiologically essential element, plays a significant role in the quality of drinking water [32]. The applicability of the proposed method for determining the concentration of Mg^{2+} ions under optimum conditions was examined with almond gum and three different water samples, including tap, stream (Yasouj City) and mineral (Sepidan company) water. The almond gum sample was prepared according to the procedure described in the experimental section. The results are presented in Table 2. The obtained results by the proposed method were found to be in excellent agreement with those obtained by AAS.

4. Conclusion

Trace amounts of Mg^{2+} ions were determined by solution scanometry as a new, simple, fast, sensitive and inexpensive detection method. In Table 3, a comparison of the characteristics of the proposed method with some of the other previously reported methods for the determination of the concentration of Mg^{2+} ions is presented. As Table 3 shows, the proposed method not only has a wider linear range but also has a reasonable limit of detection and RSD%. In addition, it is an inexpensive, simple and rapid method for determining the concentration of Mg^{2+} ions. This method is applicable for the determination

of the concentration of Mg^{2+} ions in environmental and food samples.

Acknowledgements

We gratefully acknowledge the support of Yasouj University Research for this study.

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