

DETERMINATION OF Mn²⁺ ION BY SOLUTION SCANOMETRY AS A NEW, SIMPLE AND INEXPENSIVE METHODArdeshir Shokrollahi^{a,b,*} and Nasrin Shokrollahi^{a,c}^aDepartment of Chemistry, Yasouj University, Yasouj, Iran^bRadiation and Pollution Protection Research Center of Mamasani, Mamasani, Fars, Iran^cYoung Researchers and Elite Club, Mamasani Branch, Islamic Azad University, Nourabad, Iran

Recebido em 30/01/2014; aceito em 10/08/2014; publicado na web em 08/10/2014

In this research, scanometry was used as a new, simple, fast and inexpensive method for a colorimetric determination of Mn²⁺ ion in water samples and thermocouple wire through the use of periodate reagent in an acidic medium. The results showed the oxidation of colorless Mn²⁺ ion by periodate and the formation of a purplish MnO₄⁻ ion. The system had a linear range of 1.0 to 70.0 µg mL⁻¹ Mn²⁺ ion with a detection limit of 0.314 µg mL⁻¹ and a relative standard deviation of 2.77% for G color value. This method has the capability to determine low levels of Mn²⁺ ion in thermocouple wire and water samples.

Keywords: Mn²⁺ ion; periodate; colorimetric; scanometry.**INTRODUCTION**

Manganese is a necessary trace element that exists in all active cells^{1,2} playing a crucial role in bone mineralization, protein and energy metabolism, metabolic regulation, cellular protection from injurious free radical kinds, glycosaminoglycans formation,³ human energy metabolism and processes related to the synthesis of neurotransmitters,⁴ biological system, formation of anterior pituitary hormone, vitamin B₁ and C, affecting hematopoiesis, oxidation and proteometabolism in the body.⁵ On one hand, lack of manganese can cause dermatitis, mitochondrial abnormalities, infertilities, bad formation of the bones, serum cholesterol loss, problems related to glucose metabolism and proteins and so forth.⁶

On the other hand, extra amounts of manganese can also be poisonous especially to the nervous system which appears to be the mainly unprotected⁷ part, finally leading to symptoms of Parkinson disease in adults.⁸ This element is found in rock, soil, water, little tiny soil-like portions in the air and foods such as tea, grains, rice, soya beans, eggs, nuts and cereals.^{3,9,10} Moreover, manganese compounds are used in manufacturing batteries, glass and fireworks, for whitening and sterilization purposes and as oxidants for cleaning.¹¹

Various methods for the determination of manganese are described in the reports, including inductively coupled plasma mass spectrometric method,^{4,12-19} colorimetric²⁰ and potentiometric flow injection,²¹ spectrophotometric method,^{5,22,23} flow-injection analysis (FIA),¹³ catalytic method,²⁴⁻²⁷ photometric method,^{28,29} near infrared reflectance spectroscopy,³⁰ voltammetry,^{31,32} total reflection X-ray fluorescence and ultra sound extraction.³³ However, these methods require expensive instruments, some of them requiring a number of sample pretreatments, the conducting of which is sometimes rather laborious and time consuming especially when it comes to real matrixes.

In this study scanner was used instead of spectrophotometer as a simple, fast and inexpensive method for determining Mn²⁺ ion.

Paptode was first developed by Abbaspour research group in 2006³⁴⁻³⁶ only later to be coupled with cloud point extraction procedure as a detection system by Shokrollahi group.³⁷ Recently, instead of using TLC strips used in paptode³⁴⁻³⁶ Abbaspour group has studied the solution-based method using cells for detection and determination of

dopamine^{38,39} and speciation of iron (II) and iron (III).⁴⁰

In this method the reaction is carried out in a solution in Plexiglas[®] cells or in tubes. Scanometry has some advantages; it is easy to handle and has the capability to test various compounds simultaneously, with a high scanning speed, a quick response and limited interferences. Moreover, it is inexpensive, has portable systems and unlike spectrometer, it eliminates the need to find λ_{max} . Finally more clear, symmetrical and homogenous images can be obtained through its use.

EXPERIMENTAL**Reagents and solutions**

All chemicals were of analytical grade. In addition, double distilled water was used to prepare reagents and stock solutions. A stock solution with a periodate of 0.048 mol L⁻¹ was prepared by diluting 1.10 g of metapotasium periodate (from Merck company) in a 100 mL-graduated flask by double distilled water. Mn²⁺ ion solutions were prepared by diluting 500 µg mL⁻¹ of standard solutions. A sulfuric acid of 10 mol L⁻¹ was prepared by diluting 27.2 mL of it (taken from Merck company) in a 50 mL-graduated flask by double distilled water.

Apparatus

Cells built by the sheet of Plexiglas[®] were used in this study. For the light source, a flatbed CanoScan LIDE200 with a 3-color (RGB) LED (cold cathode fluorescent lamp (CCFL)) and for the detection system, a charge couple device (CCD) were used. The horizontal and vertical resolution of the scanner was set at 300 dpi. Furthermore, the color of each cell was analyzed with software written in visual basic 6 (VB 6) for red, green and blue values. A Brand micropipette (biohit) was then used for the injection of samples into the cells. Lastly, absorbance measurements of real samples were made by a JASCO V-530, UV-Vis spectrophotometer (Hachioji, Tokiyo, Japan) equipped with 1-cm quartz cells.

Principles of red, green and blue (RGB) color systems

The RGB color system works on the basic principle of each color as a composition of red, green and blue. Colors are created by

*e-mail: ashokrollahi@mail.yu.ac.ir

adding more light to a starting black color, and for this reason it is also known as the Additive Color System. Every color in RGB spectrum is made up of a different value for each red, green and blue component, hence, its use by systems that have the ability to add lights such as LCD, CRT and RGB projectors. RGB colors range from 0 to 255, a range that a single 8-bit byte can offer through encoding 256 distinct values. In the RGB system, each color is represented in the form of (R, G, B), in which (0, 0, 0) and (255, 255, 255) refer to black and white respectively, therefore by increasing the intensity of colors, the color values will decrease. In this system 16 777 216 colors can be obtained and any color 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 color. For black and white, V is equal to 0 and 16 777 216 respectively. Through the following flowchart, R, G and B values of V for any color can be extracted:

$$R = V \text{ Mod } 256$$

$$G = ((V - R) \text{ Mod } (256^2)) / 256$$

$$B = (V - R - G \times 256) / (256^2)$$

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

It should also be mentioned that the R, G or B color value that has the same color as the solution is usually useless, as this value is often higher than 200 and does not significantly change during the experiment. In this experiment all three values of the RGB system changed therefore the one with the highest change that is "G", was chosen.

Designing the cell array

In order to make the reaction chamber, holes with an id of 1.5 cm were made in the sheet of Plexiglas with a thickness of 0.5 cm through the use of a laser beam. So as to cover the bottom of the holes and make the cells, the pierced sheet was attached to another sheet of Plexiglas® with a thickness of 0.1 cm. In our design, the cells were organized in 4 columns and 8 rows, and a total of 32 cells in the sheet.

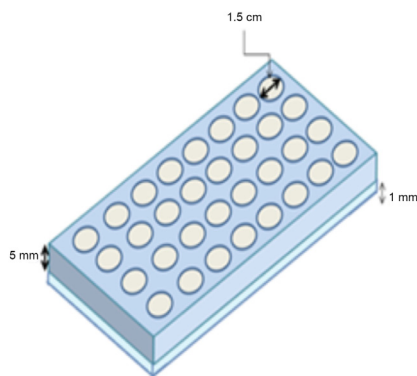


Figure 1. Cells array on the Plexiglas® sheet

In order to investigate possible leakage from neighbor cavities and cross contamination, 500 μL of violet solution with an exact concentration was injected into all cylindrical cavities in Plexiglas® sheet with no leakage and cross-contamination observed in the sheet.

General procedure

1 mL of 10 mol L^{-1} H_2SO_4 solution, 2.1 mL of 0.048 mol L^{-1} KIO_4

solution, 3-500 μL of 100 $\mu\text{g mL}^{-1}$ and 300-700 μL of 500 $\mu\text{g mL}^{-1}$ Mn^{2+} ion solution were transferred into 5 mL graduated flasks and an appropriate amount of double distilled water was added to the mark. Also a 5 mL graduated flask, with no added Mn^{2+} ion, containing 1 mL of 10 mol L^{-1} H_2SO_4 solution, 2.1 mL of 0.048 mol L^{-1} KIO_4 solution and an appropriate added amount of double distilled water was set as blank. Next, the flasks were shaken to form a homogenous solution, were carefully boiled for 30 minutes in a boiling water bath at 100 $^\circ\text{C}$ and then cooled for 5 minutes. The 500 μL portions of each solution were transferred into each cell and finally the Plexiglas® sheet was scanned with the scanner with the produced image transferred into the computer and any color change in each cell analyzed using a program written in VB 6 media. In this program, the color of each cell was analyzed based on the RGB system for obtaining R, G and B values. It should be noted that in this color analyzing program, a specific area was selected for analyzing and the number of pixels that could be indicated by this area was about 10000–300000. This program could average these pixels, therefore the noise dramatically decreased. The effective intensity for any color values was calculated as follows:

$$A_r = -\log (R_s/R_b)$$

$$A_g = -\log (G_s/G_b)$$

$$A_b = -\log (B_s/B_b)$$

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 color values of a sample and a blank, respectively.

Preparation of real samples

Water samples

1 mL of concentrated HNO_3 was added to water samples which were used after 1 hour. The procedure given in the general procedure section was then applied for analysis.

Thermocouple wire

So as to analyze thermocouple wire (Solid Chromel/Alumel (Type K)), an exact amount of wire was added to a 6 mL nitric acid and boiled for 2 minutes for a complete dissolution. The resulting solution was completely transferred to a 25 mL flask and dilute to the mark. The obtained solution was lastly analyzed according to the described procedure.

RESULTS AND DISCUSSION

The aim of this work was to develop a simple, fast and inexpensive method for a colorimetric determination of trace amounts of Mn^{2+} ion in water samples and thermocouple wire through the use of periodate as oxidizing reagent. In this regard, the influence of various effective parameters, including heating and cooling time and the concentration of chemical reagents were optimized.

Effect of H_2SO_4

Optimizing the concentration of sulfuric acid is one of the main steps in optimization. This is because manganese has different oxidation forms (namely Mn II and Mn VII, Mn IV and Mn VI) each of which is stable in neutral, acidic and basic environments respectively. Worth mentioning is the fact that sulfuric acid concentration has a large influence on the sensitivity and efficiency of the method.

To study the effect of sulfuric acid, solutions containing 500 μL of Mn^{2+} ion (500 mg L^{-1}) and 2.1 mL of periodate (0.048 mol L^{-1}) and different concentrations of sulfuric acid (0.1–3.0 mol L^{-1}) were

prepared according to the procedure. 500 μL of each sample was then transferred into the cells and after scanning the cells, the image of each cell was analyzed with the software as illustrated in Figure 2. As this Figure shows, with the increase in the concentration of H_2SO_4 , the G value increased, the intensity of violet decreasing, from 2.0 mol L^{-1} concentration onwards, hence 2.0 mol L^{-1} was selected as the optimum concentration for H_2SO_4 . Because the highest value belonged to parameter G, it was utilized as the original one.

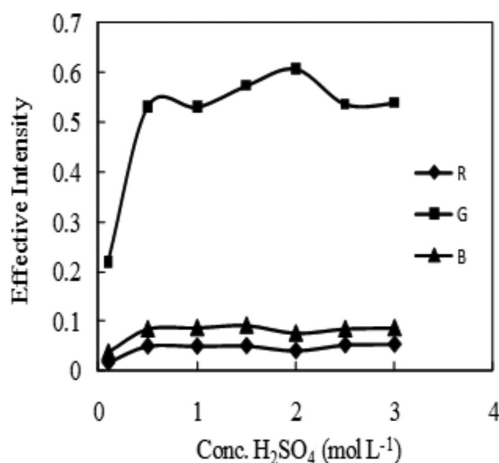


Figure 2. Effect of H_2SO_4 amount on reaction (Conditions: 500 μL Mn^{2+} ion (500 mg L^{-1}) + 2.1 mL KIO_4 (0.0478 mol L^{-1}) + 0.1–3.0 mol L^{-1} H_2SO_4 + 30 minutes heating and total volume of 5 mL)

Effect of KIO_4

The optimization of the concentration of KIO_4 as an oxidizing reagent was the main step of optimization. To study the effect of this reagent, solutions containing 500 μL of Mn^{2+} ion (500 mg L^{-1}) and 1.0 mL of sulfuric acid (10 mol L^{-1}) and different concentrations of periodate (0.001–0.03 mol L^{-1}) were prepared according to the procedure. Next, 500 μL of each sample was transferred into each Plexiglas[®] sheet. After scanning the cells, the image of each cell was finally analyzed with the software. The obtained results are illustrated in Figure 3. As this Figure shows, the G value increased with the increase in the concentration of KIO_4 and decreased from the concentration of 0.02 mol L^{-1} onwards. Moreover, the redox reaction was completed with high rather than low amounts of KIO_4 .

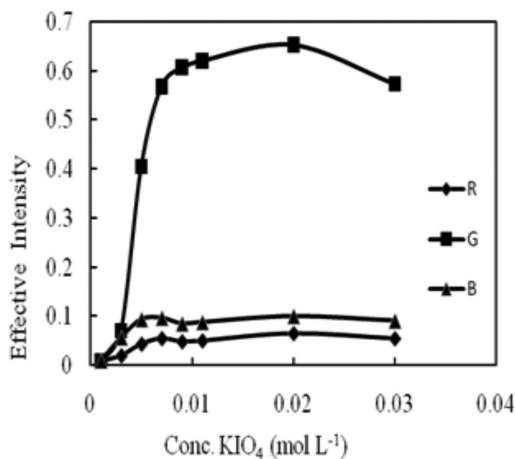


Figure 3. Effect of periodate amount on the reaction (Conditions: 500 μL Mn^{2+} ion (500 mg L^{-1}) + 1.0 mL H_2SO_4 (10 mol L^{-1}) + 0.001–0.03 mol L^{-1} KIO_4 + 30 minutes heating and total volume of 5 mL)

Effect of heating time

The effect of temperature and duration of heating are two important parameters on the completion of the reaction. The reaction was completed at high temperatures. Figure 4 illustrates that the effective intensity is the highest when the period of heating is 30 minutes. This effect clearly indicates that all Mn^{2+} ions reacted with IO_4^- and the effective intensity reached a maximum value.

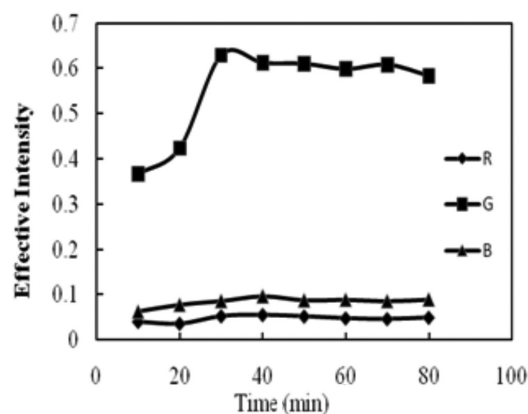


Figure 4. Effect of heating time on the reaction (Conditions: 500 μL Mn^{2+} ion (500 mg L^{-1}) + 1.0 mL H_2SO_4 (10 mol L^{-1}) + 2.1 mL KIO_4 (0.0478 mol L^{-1}) + 10–80 minutes heating and total volume of 5 mL)

Effect of cooling time

To study the effect of cooling time, a solution containing 500 μL of Mn^{2+} ion (500 mg L^{-1}), 2.1 mL of periodate (0.048 mol L^{-1}) and 1.0 mL sulfuric acid (10 mol L^{-1}) was prepared according to the procedure. 500 μL of the sample was then transferred into the cells and was scanned for 5–60 minutes. After scanning the cells, their images were analyzed with the software, the results being illustrated in Figure 5. It is seen that the effective intensity is independent of cooling time in the duration of 5–60 minutes therefore the minimum time i.e. 5 minutes was selected for the aforementioned steps.

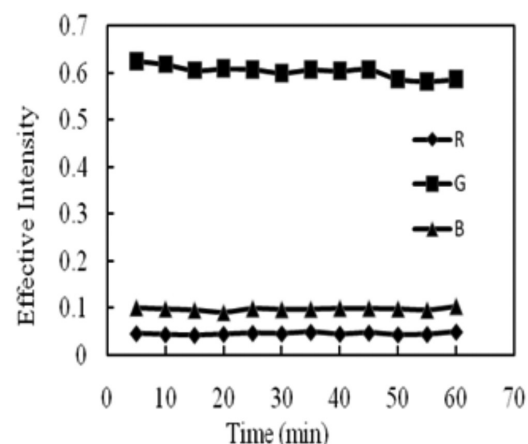


Figure 5. Effect of cooling time on the reaction (Conditions: 500 μL Mn^{2+} ion (500 mg L^{-1}) + 1.0 mL H_2SO_4 (10 mol L^{-1}) + 2.1 mL KIO_4 (0.0478 mol L^{-1}) + 30 minutes heating and total volume of 5 mL)

Analytical performance

Figure 6 illustrates the calibration curve under optimum conditions. In the range of 1.0–70.0 $\mu\text{g mL}^{-1}$, a proper linear relationship was obtained between the effective intensity of the product and the

concentration of Mn^{2+} ion. The equation for the regression line was $Y=0.0145X-0.0146$ (for G), where C is the concentration of Mn^{2+} ion in $\mu g mL^{-1}$.

In order to render the reproducibility of the method, 6 sample solutions of $50 \mu g mL^{-1}$ Mn^{2+} ion were analyzed and 2.77 was the RSD% (Relative Standard Deviation) for G color values. The detection limit was obtained $0.314 \mu g mL^{-1}$ based on the standard deviation of 8 blanks.

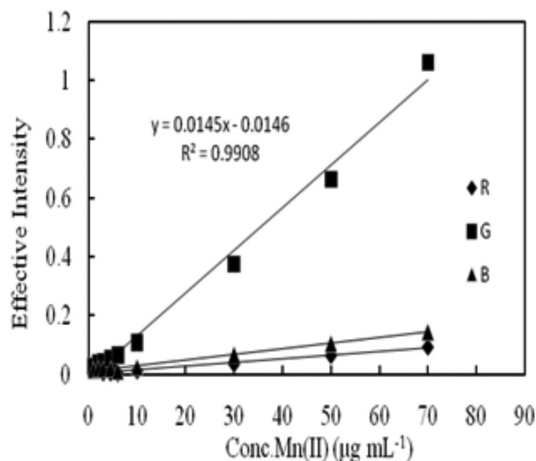


Figure 6. Calibration curve for determination of Mn^{2+} ion (Conditions: 1.0-70 $mg L^{-1}$ Mn^{2+} ion + 1.0 mL H_2SO_4 (10 $mol L^{-1}$) + 2.1 mL KIO_4 (0.0478 $mol L^{-1}$) + 30 minutes heating and total volume of 5 mL)

Interference study

To study the selectivity of the proposed method in determining Mn^{2+} ion, the effect of various species on the determination of $50 \mu g mL^{-1}$ Mn^{2+} ion was tested under optimum conditions. The tolerance limit was defined as the concentration of added ion that causes less than $\pm 5\%$ the relative error of G value. The results are shown in Table 1.

In this method, most of the species do not interfere, because the scanometry is based on the reflective properties of the samples. It

Table 1. Effect of interfering species in the determination of $50 \mu g mL^{-1}$ Mn^{2+} ion in the optimum conditions

Interfering species	Added as	Tolerance Conc. ($\mu g mL^{-1}$)
Fe^{3+} , Al^{3+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Na^+ , Li^+	Nitrate salt	5000
ClO_4^- , $Cr_2O_7^{2-}$, NO_3^-	Sodium or Potassium salt	5000
La^{3+} , Mg^{2+} , Zn^{2+} , Co^{2+}	Nitrate salt	3000
Cr^{3+}	Nitrate salt	1000
Zr^{4+} , Bi^{3+} , Hg^{2+} , Ag^+	Choloride salt of Zr^{4+} , Nitrate salt of Bi^{3+} , Hg^{2+} and Ag^+ ions	500

is notable that by this method colored species such as Cr^{3+} , $Cr_2O_7^{2-}$, Cu^{2+} and Ni^{2+} ions or the product of reaction between the interference and reagent (which changes the value of R, B or both parameters but not the G value), do not interfere in the determination of manganese.

Application

The applicability of the method in determining Mn^{2+} ion by the standard addition technique and recovery was examined with thermocouple wire (Solid Chromel / Alumel (Type K)) and six different water samples including tap water, water falls, mineral water, river water, canal water and hot spring.

The thermocouple wire sample was prepared according to the experimental section and its manganese percentage was determined by the proposed method and was compared with UV-Vis method. The results are summarized in Table 3.

The determination of Mn^{2+} ion in the thermocouple wire sample is remarkably accurate by the proposed method.

CONCLUSIONS

Scanometry as an easy, safe, rapid and inexpensive method has recently been used for the determination of trace amounts of

Table 2. Characteristics of the standard addition curves and recovery percentage, for determination of Mn^{2+} ion in water samples

sample	Regration equation	R^2	Added ($\mu g mL^{-1}$)	Found ($\mu g mL^{-1}$)	Recovery %
Tap water (Yasouj city)	$A=0.013X-0.044$	0.988	00.00	Nd ^a	---
			20.00	19.99	99.95
			40.00	39.64	99.10
Water falls (Yasouj city)	$A=0.014X-0.050$	0.969	00.00	Nd	---
			20.00	20.02	100.10
			40.00	40.01	100.00
Mineral water (Satrap)	$A=0.014X-0.058$	0.966	00.00	Nd	---
			20.00	20.20	101.00
			40.00	40.01	100.00
River water (Mamasani city)	$A=0.013X-0.034$	0.977	00.00	Nd	---
			20.00	19.95	99.75
			40.00	39.78	99.45
Canal water (Mamasani city)	$A=0.013X-0.026$	0.985	00.00	Nd	--
			20.00	19.60	98.00
			40.00	40.56	101.40
Hot spring (Mamasani city)	$A=0.009X-0.003$	0.997	00.00	Nd	---
			20.00	20.06	100.30
			40.00	40.34	100.90

Nd: Not detected.

Table 3. Determination of manganese percentage in thermocouple wire

Sample	Found by method	
	Scanometry	Uv-Vis
Thermocouple wire	1.50%	1.57%

analysts.^{36,38,39,41,42} In this study, scanometry was used for the determination of Mn²⁺ ion. This method has been developed as an alternative to visible spectrophotometry and the analytical results showed that it can be successfully adopted in determining Mn²⁺ ion with high selectivity in real samples.

ACKNOWLEDGEMENTS

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

REFERENCES

- Oga, S.; *Fundamentos de Toxicologia*, Atheneu: São Paulo, **2008**.
- Goldhaber, S. B.; *Regul. Toxicol. Pharmacol.* **2003**, *38*, 232.
- Williams-Johnson, M.; *Concise International Chemical Assessment Documents 12*, 1999.
- Amais, R. S.; Donati, G. L.; Nebrega, J. A.; *Anal. Chim. Acta* **2011**, *706*, 223.
- Wei, Q.; Yan, L.; Chang, G.; Ou, Q.; *Talanta* **2003**, *59*, 253.
- Agency for Toxic Substances and Disease Registry; *Toxicological profile for manganese (update)*. Atlanta, Georgia, 2000: Agency for Toxic Substances and Disease Registry, A-3 to A-5.
- Erikson, K. M.; Thompson, K.; Aschner, J.; Aschner, M.; *Pharmacol. Ther.* **2007**, *113*, 369.
- Garcia, S. J.; Gellein, K.; Syversen, T.; Aschner, M.; *Toxicol. Sci.* **2007**, *95*, 205.
- Mckenzie, H.A.; Smythe, L.E.; *Quantitative Trace Analysis of Biological Materials*, Elsevier: Amsterdam, **1988**.
- Ferreira, S. L. C.; Souza, A. S.; Brando, G. C.; Ferreira, H. S.; Dos Santos, W. N. L.; Pimentel, M. F.; Vale, M. G. R.; *Talanta* **2008**, *74*, 699.
- Banta, R. G.; Markesbery, W. R.; *Neurology* **1977**, *27*, 213.
- Bezerra, M. A.; Maeda, S. M. N.; Oliveira, E. P.; Carvalho, M. F. B.; Santelli, R. E.; *Spectrochim. Acta* **2007**, *62*, 985.
- Tang, B.; Han, F.; *Anal. Lett.* **2001**, *34*, 1353.
- Yebra, M. C.; Moreno-Cid, A.; *Anal. Chim. Acta* **2003**, *477*, 149.
- Coskun, N.; Akman, S.; *Talanta* **2004**, *64*, 496.
- Tokman, N.; Akman, S.; Ozeroglu, C.; *Talanta* **2004**, *63*, 699.
- Wagatsuma, K.; Kodama, K.; Park, H.; *Anal. Chim. Acta* **2004**, *502*, 257.
- Cozzolino, D.; Moron, A.; *Anim. Feed Sci. Technol.* **2004**, *11*, 161.
- Lemos, V. A.; Baliza, P. X.; Carvalho, A. L.; Oliveira, R. V.; Teixeira, L. S. G.; Bezerra, M. A.; *Talanta* **2008**, *77*, 388.
- Mehlig, J. P.; *Ind. Eng. Chem.* **1939**, *11*, 274.
- Ohura, H.; Ishibashi, Y.; Imato, T.; Yamasaki, S.; *Talanta* **2003**, *60*, 177.
- Motojima, K.; Hashitani, H.; Imahashi, T.; *Anal. Chem.* **1962**, *34*, 571.
- Fathi, M. R.; Hashemi, P.; Abolhasan-Oghly, M. J.; *J. Chin. Chem. Soc.* **2007**, *54*, 1253.
- K. Mutafchiev; *Anal. Lett.* **2001**, *34*, 1401.
- Pourreza, N.; Kamran-HeKani, S.; Rastegarzadeh, S.; *Can. J. Anal. Sci. Spectrosc.* **1998**, *43*, 149.
- Kang, W.; Zhou, F. L.; Deng, X. P.; *Journal of East China Geological Institute* **1997**, *20*, 141.
- Shi, T.Q.; Huang, J. G.; Qiu, C. Q.; *Chin. J. Anal. Lab.* **1998**, *17*, 34.
- Waldbauer, L.; Ward, N.; *Ind. Eng. Chem.* **1942**, *14*, 727.
- Johnson, D. A.; Lott, P. F.; *Anal. Chem.* **1963**, *35*, 1705.
- Filipe, M. S.; Christopher, M. A.; *Talanta* **2003**, *61*, 643.
- Baytak, S.; Rehber Turker, A.; *Turk. J. Chem.* **2004**, *28*, 243.
- Zhang, F.; *Talanta* **2003**, *60*, 31.
- Alvarez, J.; Marco, L. M.; Arroyo, J.; Greaves, E. D.; Rivas, R.; *Spectrochim. Acta* **2003**, *58*, 2183.
- Abbaspour, A.; Mehrgardi, M. A.; Noori, A.; *Sens. Actuators* **2006**, *113*, 857.
- Abbaspour, A.; Khajehzadeh, A.; Noori, A.; *Anal. Sci.* **2008**, *28*, 721.
- Abbaspour, A.; Mirahmadi, E.; Khajehzadeh, A.; *Anal. Methods* **2010**, *2*, 349.
- Shokrollahi, A.; Abbaspour, A.; Azami Ardekani, Z.; *Anal. Methods* **2012**, *4*, 502.
- Abbaspour, A.; Valizadeh, H.; Khajehzadeh, A.; *Anal. Methods* **2011**, *3*, 1405.
- Abbaspour, A.; Khajehzadeh, A.; Ghaffarinejad, A.; *Analyst* **2009**, *134*, 1692.
- Abbaspour, A.; Khajehzadeh, A.; Ghaffarinejad, A.; *Anal. Methods* **2011**, *3*, 2268.
- Shokrollahi, A.; Roostan, T.; *Anal. Methods* **2013**, *5*, 4824.
- Shokrollahi, A.; Mohammadpour, Z.; Abbaspour, A.; *Pharm. Chem. J.*, in press.