

(RESEARCH ARTICLE)



Determination of cerium (IV) by continuous flow injection and sequential flow injection methods

Mohammed Nawfal Abdul Maged *

Department of Chemistry, College of Education for Pure Science, University of Kerbala Iraq.

Open Access Research Journal of Science and Technology, 2025, 13(01), 085-091

Publication history: Received on 27 December 2024; revised on 18 February 2025; accepted on 21 February 2025

Article DOI: <https://doi.org/10.53022/oarjst.2025.13.1.0035>

Abstract

The research aims to design a new flow injection system using the two continuous and successive techniques for the determination of cerium quaternary, through the interaction of cerium quaternary with potassium iodide in an acidic medium and the liberation of yellow-colored iodine, which gives a maximum absorption peak at the wavelength is 353 nm. The method includes manufacturing a quadruple valve from cheap materials and choosing the optimal system design with studying the optimal conditions for the system, which include potassium iodide concentration, acid concentration, Pump speed, acid volume, pattern size, reaction profile length, then designing a new sequential injection system and selecting the optimal design for it. The flow injection method yielded compliance with Beer-Lambert law in the range (1-40 mg/L). And a correlation coefficient (R²) of 0.997, and a dilution coefficient equal to 1.33 and 1.32 for concentrations of 10 and 30 mg / L, respectively. The sequential injection method also gave a clear improvement in the height of the apex and an increase in sensitivity.

Keywords: Flow injection system; Absorption peak; Cerium; Element

1. Introduction

In 1975 saw the discovery of the flow injection technique by Ruzicka and Hansen in Denmark [1] and by Stewart and his associates in America [2]. with remarkable speed, sensitivity to chemical analyses, and great efficiency in an automated or semi-automated manner [3–4]. In this technique, a liquid sample is injected into a suitable carrier solution that moves continuously and indivisibly. The injected sample then moves to the reaction coil for mixing and product formation, and finally to the detector, which continuously records the electrode potential, absorbance, or any other physical factor that changes as the sample material passes through the Flux cell [6,5]. As for the technique of successive injection analysis (SIA), it is one of the methods derived from the analysis by flow injection. The principles of this technique were developed (Ruzicka, Marshal) [7] in 1990. By controlling the quick change in the direction of the carrier current flowing backwards and then forwards until a complete reaction is obtained, it is pushed forward so that the sample reaches the detector sooner after achieving the best mixing and reaction completion in the loading file. [8] Microquantities of materials are consumed in this technology, and the optional or selective valve takes the place of the injection valve because it allows for the selection of various models and flow streams, as well as simple branched flow pipes. These benefits all contributed to the SIA technology's adaptability and ease of use in chemical systems. (10,9) Cerium is a lanthanate element, symbol Ce and atomic number 58, discovered in 1839 by Mosander. [12,11]. It is one of the rare earth's metals, and it is one of the most important and widespread elements of the anthanes on the earth's crust [13,14]. Cerium is found in nature with the rest of the lanthanate elements in the mineral's allanite, bastnaite, monazite, cerite and samarskite, and allanite and monazite are important sources of cerium commercially [15, 16]. Cerium metal is very effective and a strong oxidizing agent, so it is stable when combined with oxygen [17]. Cerium has three oxidation states (II), (III), (IV), where the oxidative state (II) is the rarest case for it, while the last two cases are the most common, especially the case (IV), which behaves as a strong oxidizing agent in aqueous solutions [11, 12]. Cerium is an important element in industry and is used in nuclear reactors and in alloys with nickel and chromium. It is also used in the

* Corresponding author: Mohammed Nawfal Abdul Maged.

manufacture of lasers [20, 19, 18], fluorinated materials and magnets [21]. Cerium has a major role in industrial products, as it is used in the manufacture of carbon and ceramic arc lamps and is used as an additive to diesel fuel [13]. Cerium has a role in medicine, as it is used as an antiseptic agent in the treatment of skin burns [22, 23] and in the treatment of high temperatures [24], and cerium salts are used to treat vomiting during pregnancy and depression, and it is also used as an antiseptic and astringent [25]. Cerium has an important effect on growth and the functions of the blood, nervous system, hair, liver, heart, bones and brain [26]. Environmental studies of cerium increased due to the widening of agricultural and industrial applications in which cerium enters, especially when it is used as an additive to diesel engine fuel, which causes an increased risk of human exposure to cerium. The general population can be exposed to cerium mainly through oral intake through food and through breathing [28,27]. Cerium was determined by various methods, including using the flow injection method [29,30, 31], and spectrophotometric methods using organic reagents such as 2-Methyl -4- (3,4- dihydroxy phenyl) thiazole hydrochloride [32], 2,4-dihydroxy benzophenone benzoic hydrazone [33], Leuco Xylene Cyanol FF [34], Arsenazo III [35], propionyl promazine phosphate (PPP) [36], pyridine-2,6-diol [37], pyrogallol red [38]. Cerium was determined by other methods such as ICP [39], ICP-AES [41, 40], electrolytic determination by manufacturing selective electrodes [43, 42], mercury dripping electrode [44], and fluorescence [46, 45]

1.1. Equipment and materials used

1.1.1. Devices used

UV-visible spectrophotometer (Shimadzu, Japan), Reaction coil made from glass, I.D=0.5mm) Local made,) Quaternary Valve (Local made), Peristaltic Pump (Heidolph, Pump drive 5001, Germany), Hot Plats (Ardeas 51), Kompensog Graph (Siemens C 1032) , Balance (Denver Instrument) , pH-Meter (WTW,pH720,Germany) , Sample loop made from Teflon (1 mm I.D) and Thermometer.

1.1.2. Materials used

Ce^{4+} solution was prepared at a concentration of (1000 mg/L) by dissolving 0.3812 g of ammoniated ceric nitrate in 100 ml of distilled water containing 0.5 ml of nitric acid. A potassium iodide solution was prepared at a concentration of (0.3 mol/l) by dissolving 7.2 g of potassium iodide in 250 ml of distilled water. Sulfuric acid (1 mol/L) was prepared by taking 5.42 ml of the acid and diluted to 100 ml with distilled water.

2. Design of the continuous flow injection system

A flow injection system was designed consisting of a peristaltic pump, a locally manufactured quadruple valve, a locally manufactured glass reaction coil (R.C), and the detector, which is a spectrophotometer (D), and a recorder (R). After studying the optimal design of the system, it was found that the design in Figure (1) is the optimal design for the system, where potassium iodide was chosen as a carrier and both the acid and the sample were loaded through the valve, Figure (1).

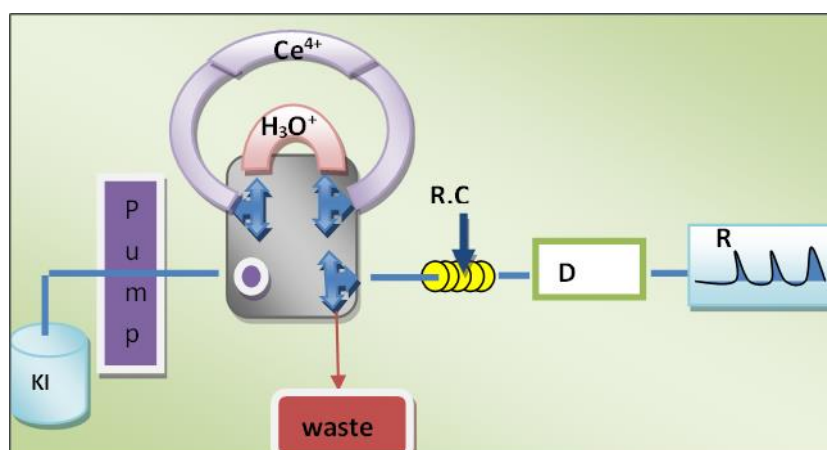


Figure 1 Components of the continuous flow injection system

3. Study the optimal conditions for the system

The optimal conditions for the system were studied, including potassium iodide concentration, acid concentration, pump speed, reaction coil length, acid joint length (acid volume), pattern joint length (sample volume). Table (1) shows the optimal conditions that were chosen for the work of the system.

Table 1 Optimal conditions for the continuous flow injection system

Variants	optimal conditions	summit height			mean	S.D	R.S.D%
KI	0.3 mol / L	0.800	0.740	0.740	0.760	0.020	2.760
H3O ⁺	1 mol / L	0.800	0.740	0.800	0.783	0.062	7.800
Pump Speed	2.2 ml / min	0.950	0.850	0.800	0.866	0.040	4.600
Length of R.C	100 cm	0.950	0.850	0.800	0.866	0.040	4.600
Volume of H3O ⁺	197.25ML	0.950	0.950	0.950	0.950	0.000	0.000
Volume of Ce ⁴⁺	157 ML	0.950	0.950	0.950	0.950	0.000	0.000

4. Preparing the calibration curve for the continuous flow injection system

A series of concentrations ranged between (0.5 - 50 mg / L), where the results were linear between (1 - 40 mg / L) and as shown in Table (2) and Figure (2), and the detection limit was (0.5) mg / L and a correlation coefficient R = 0.997.

Table 2 the values of the standard curve of his system FIA

Con.of Ce ⁴⁺ ppm	Peak High in cm			Mean	S.D	R.S.D%
1	0.050	0.050	0.050	0.050	0.000	0.000
5	0.150	0.150	0.150	0.150	0.000	0.000
10	0.300	0.300	0.300	0.300	0.000	0.000
20	0.600	0.550	0.500	0.550	0.050	4.000
30	0.800	0.800	0.800	0.800	0.000	0.000
40	1.000	1.050	1.000	1.017	0.029	1.690

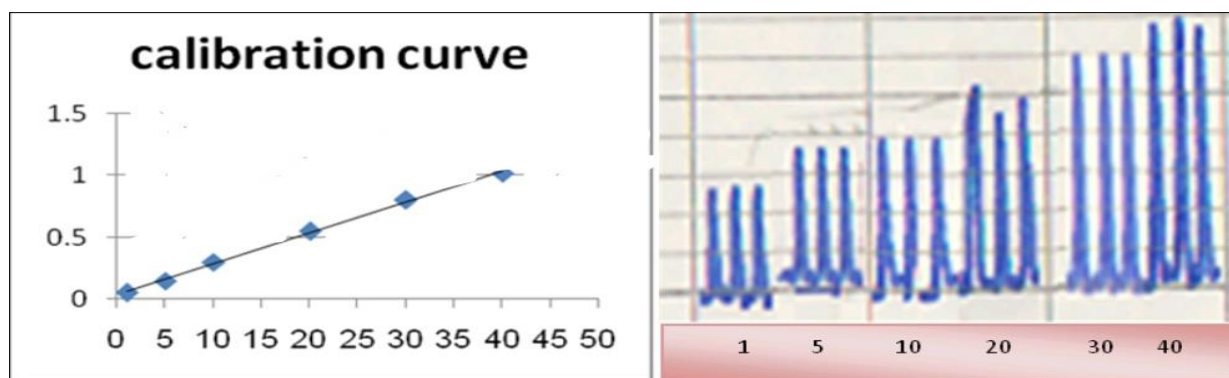


Figure 2 Standard curve for injection analysis

5. Study the dispersion coefficient

In order to determine the degree of dilution that occurred to the solutions throughout their presence in the system from the time of injection until the result is recorded by the detector, one of the most crucial studies in the flow injection

technique is the dispersion coefficient. The dilution coefficient D , which can be calculated using the following formula, can be used to express the degree of dilution [48,47].

$$D = H^{\circ} / H_{\max}$$

In the case of a reaction conducted outside of the flow injection system, the height of the apex without dilution is denoted by H° , whereas the peak height with dilution is denoted by H_{\max} . Figure (3) illustrates that the dilution coefficient, which was determined during the investigation for two doses of 10 and 30 mg/L, was 1.33 and 1.32, respectively.

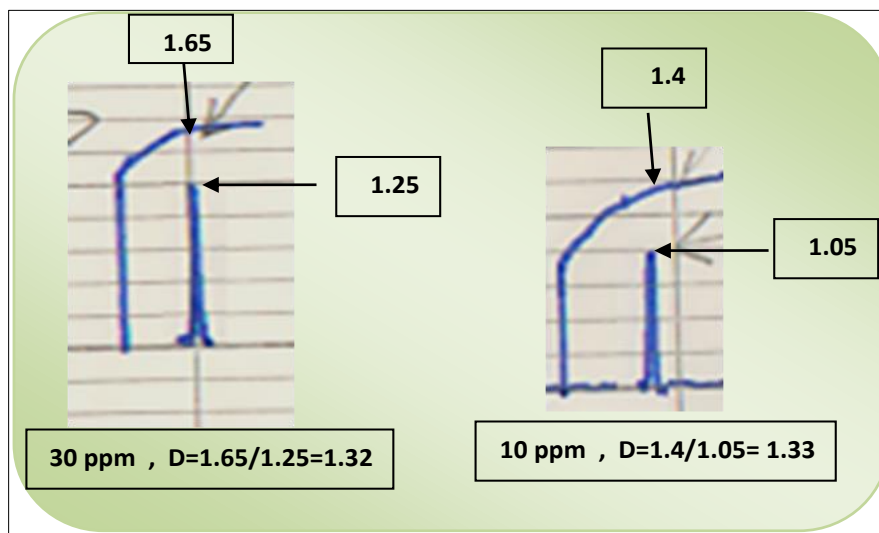


Figure 3 Dilution coefficient

6. Designing a sequential injection analysis system

One of the drawbacks of flow injection is the dilution that occurs for solutions from the beginning of injection to the arrival of the sample to the detector, and to overcome this factor (Ruzicka, Marshal) [7] in the year (1990) developed the principles of this technique., an injection analysis system was designed successively, as shown in Figure (4).

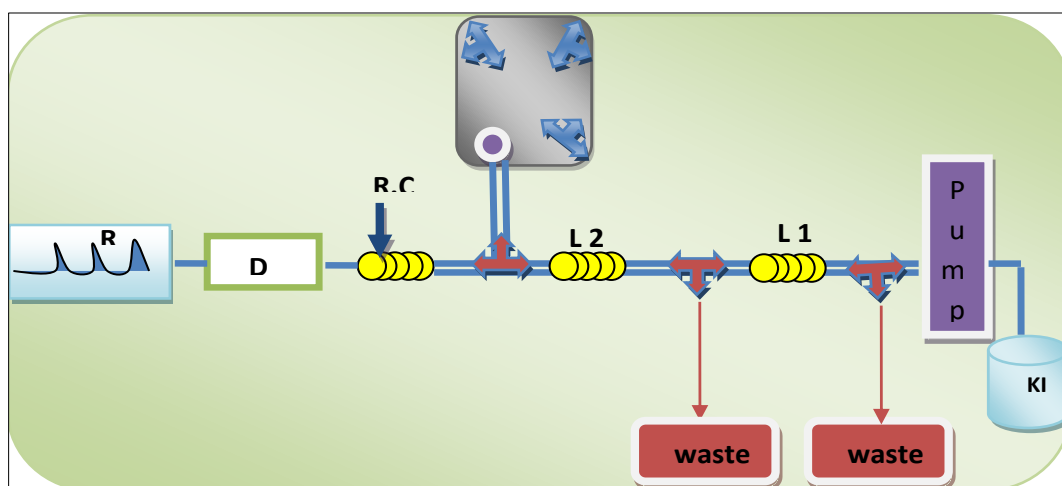


Figure 4 The successive injection system

from Figure (4) it is noted that two designs can be developed for the system (B, A) with the acid loading location and the sample does the acid carry in (L 1) and the model in (L 2) or vice versa, as shown in Figure (5). From the results, it became clear that design (B) gave better results.

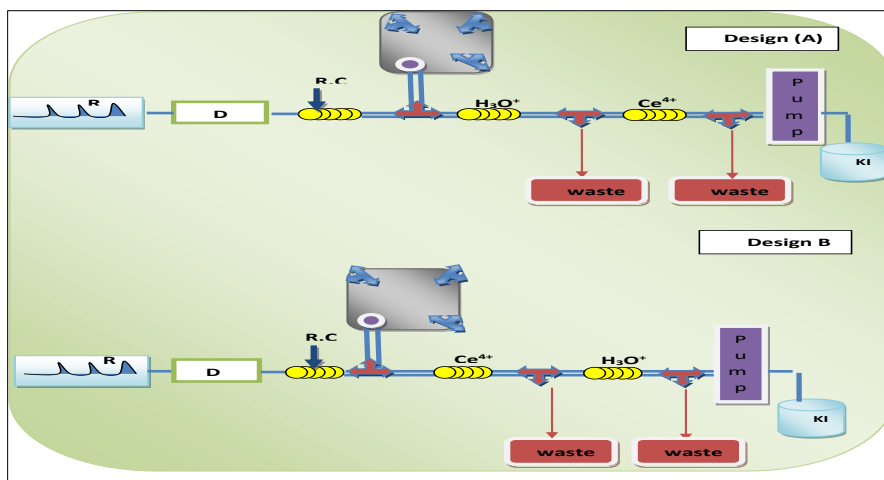


Figure 5 Design A and Design B of the successive injection system

6.1. Preparing the calibration curve for the successive injection system:

A series of concentrations were prepared, ranging between (0.5 - 50 mg/L), where the results were linear between (1 - 40 mg/L), as shown in Table (2) and Figure (2), and the limit of detection was (0.5) mg / liter and a correlation coefficient R (0.997). When comparing Table (3) with Table (2), we notice the clear improvement of the peak height. There was also a clear improvement in the sensitivity of the method, as shown in Figure (5).

Table 4 the values of the standard curve of his system SIA

Con. Of H ₃ O ⁺ (M)	Peak High in cm			Mean	S. D	R.S.D%
1	0.100	0.100	0.100	0.100	0.000	0.000
5	0.250	0.200	0.200	0.216	0.026	2.700
10	0.400	0.400	0.400	0.400	0.000	0.000
20	0.750	0.700	0.750	0.730	0.029	1.800
30	1.000	1.000	1.000	1.000	0.000	0.000
40	1.350	1.350	1.350	1.350	0.000	0.000

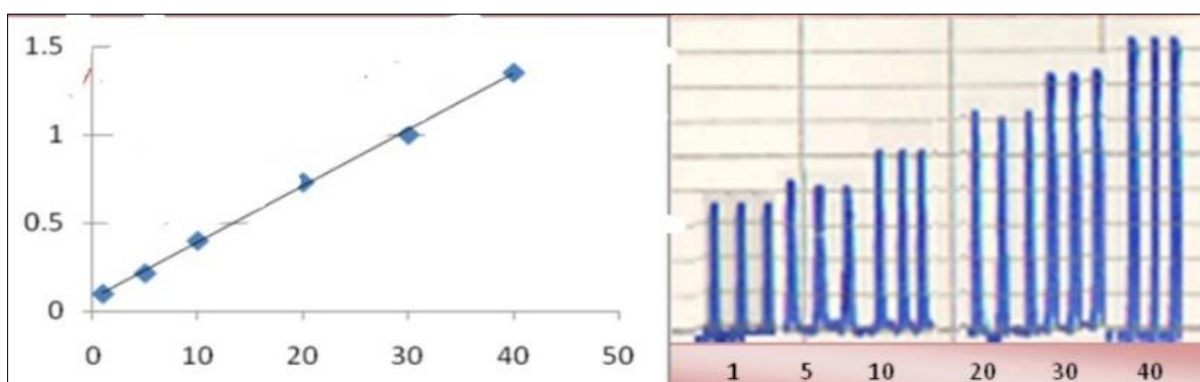


Figure 6 Standard curve for successive injection analysis

7. Conclusion

- Manufacture of a new flow injection valve from cheap materials available in the markets comparable to the valves manufactured globally. It contains four valves and has the capacity to load two materials of a known size.

Therefore, it can be used in chemical reactions consisting of three materials or less, as it was used in this system and gave a very high repetition.

- Designing a new flow injection unit using both continuous and sequential techniques, where these two techniques can be used to estimate quaternary cerium, with speed of up to 40 samples per hour, with high frequency, a wide linear range, with the lowest dispersion rate and the lowest cost.

References

- [1] J. Ruzicka, E.H. Hansen, "Flow Injection Analysis. Part I. A new concept of fast continuous flow analysis". *Analytical chemical Acta*, 78, 145-157, (1975).
- [2] M. Troanowicz, "Flow Injection Analysis, Instrumentation and applications", 1st. ed. World Scientific Publishing USA, (2000).
- [3] D. Barceló, "Comprehensive Analytical Chemistry. Advances in Flow Injection Analysis and Related Techniques", Edited by Spas D. Kolev, 1st ed, Elsevier, Australia (2008).
- [4] G. Vurck, *Anal. chem. Acta.* 14, 288 (1981).
- [5] J.M. Calatayud, "Flow Injection Analysis of pharmaceuticals", university of Valencia, Spain, Taylor and Francis, (2003).
- [6] Gary D. Christian, "Analytical Chemistry", 6th ed, John Wiley & sons Ltd, P.665, (2004).
- [7] J. Ruzicka, G.D. Marshall, G.D. Christian, *Analytical chemistry*, 62, 1861-1866, (1990).
- [8] J. Ruzicka, G.D. Marshall, *Analytical chem. Acta*, 237, 329-343, (1990).
- [9] S.B. AL-Badvi, M.Sc., Thesis, Baghdad university (2002).
- [10] V. E. Dutt, H. A. Mottola, *Anal. Chim.*, 49(6), P. 776 (1977).
- [11] T. Moeller, "The Chemistry of Lanthanides", Pergamon, Texts in inorganic chem., 26, p. (47,89), (1973).
- [12] S. Hamdi, R. Siab and Bonnet, *Lebanese Sci.J.*, 10, 2 (2009).
- [13] MA. Boston, "Health Effects Institute. Evaluation of human risk from cerium added to diesel fuel", USA Health Effects Institute, Communication 9, (2001).
- [14] B. James Hedrick, "Rare earth minerals year book", U.S. Geological Survey, Mineral Commodity Summaries. (2004). Available online at [http://minerals.usgs.gov/minerals/pubs/commodity/rare earth](http://minerals.usgs.gov/minerals/pubs/commodity/rare%20earth).
- [15] DR. Lide, "CRC handbook of chemistry and physics", 86th ed., Boca Raton, CRC Press, P.4-48, (2005).
- [16] MJ. O'Neil; *The Merck index: an encyclopedia of chemical, drug, and biologicals*, 13th ed., Whitehouse Station, NJ: Merck and Co., P.89, 342-385. (2001)
- [17] BT. Kilbourn, "Cerium and cerium compounds", *Kirk-Othmer encyclopedia of chemical technology*, New York, John Wiley and Sons, (2003).
- [18] F.W. Oehme, "Toxicity of Heavy Metals in the Environment", Marcel Dekker, New York and Basel, P.169, (1979).
- [19] S. An Abbasi, "Spectrophotometric determination of trimipramine using cerium (IV) sulphate (IV) potassium idate (VII)", *Int J, Environ Anal. Chem*, 34, P.181-187, (1998).
- [20] F.A. Cotton, G. Wilkinson, "Advance Inorganic Chemistry", Wiley Eastern, New Delhi, (1976).
- [21] S. Hirano, KT. Suzuki, "Exposure, metabolism, and toxicity of rare earths and related compounds", *Environ Health Perspect*, P.85-95, (1996).
- [22] WW. Monafo, SN. Tandon, VH. Ayvazian, J. Tuchschildt, AM. Skinner, F. Deitz, "Cerium nitrate: a new topical antiseptic for extensive burn", *Surgery*, 80, P.465-73, (1976).
- [23] MA. Jakupec, P. Unfried, BK. Keppler, "Pharmacological properties of cerium compounds", *Rev Physiol Biochem Pharmacol*, 153, P.101-11, (2005).
- [24] SN. Kale, S. Arora, KR. Bhayani, KM. Paknikar, M. Jani, UV. Wagh, et al, "Cerium doping and stoichiometry control for biomedical use of La_{0.7}Sr_{0.3}MnO₃ nanoparticles: microwave absorption and cytotoxicity study", *Nanomedicine*, 2, P.217-21, (2006).

- [25] B. Li, Y. Sun, M. Yin, "Spectrophotometric determination of certain cephalosporins through oxidation with cerium (IV) and 1-chlorobenzotriazole", *J Anal Atomic Spect*, 14, P.1843-1846, (1999).
- [26] Li. Jingmei, WEI. Wentao, "Catalytic Kinetic spectrophotometric determination of cerium", *J. of the Rare Earth*, 28, No.3, P.387-390, (2010).
- [27] O. Wappelhorst I. Kuehn, H. Heidenreich, B. Markert, "Transfer of selected elements from food into human milk", *Nutrition*, 18, P.316-22, (2002).
- [28] P. Roth, N. Mohlo, D. Taylor, J. McAughey, K. Henrichs, "Assessment of internal dose from radionuclides using stable isotope tracer techniques in man". CEC Radiation Protection Programme 1990-1992, Contract No. B17-0029, Contract Report, (1992).
- [29] Y. Rao, X. Zhang, G. Luo and W.R.G. Baeyens, *Anal.Chim. Acta*, 396, 2, P. 273-277, (1999).
- [30] K.H. Al-sowdani and A. Townsend, *Anal.Chim. Acta*, 179, P. 469-473, (2002).
- [31] X. Zhu, Y. Zhang, A. Gong and X. Zhang, *Spect.Lett.*, 41,5, P. 237-241, (2008).
- [32] Ahmed Sadoon Abbas, "Spectrophotometric Determination of Bismuth (III), Cerium (IV) and Vanadium (V) Using an Organic Reagent 2-Methyl -4- (3,4-dihydroxy phenyl) thiazole hydrochloride", M.Sc. Theses, Babylon University, (2011).
- [33] C. Keshava Rao, V.K. Reddy, and T.S. Reddy, "Rapid and Sensitive spectrophotometric determination of cerium (IV) with 2,4-dihydroxy benzophenone benzoic hydrazone", *Talanta*, P.237-241, (1994).
- [34] Hosakere D. REVANASIDDAPPA and Telangusadhushetty N. KIRAN KUMAR, "Spectrophotometric Determination of Cerium with Leuco Xylene Cyanol FF", *The Japan Society for Analytical Chemistry*, Vol.18, P1275-1278, (2002).
- [35] E. Bobrowska-Grzesik, A.M, A.M, A.M, A.M, A.M. Grossman, and J. Ciba, *Fresenius J. Anal. Chem.*, 345,614, (1993).
- [36] S.P. Masti, J. Seetharamappa, M.B. Melwanki and N. Motohashi, "spectrophotometric determination of cerium (IV) using a phenothiazine derivative", *Anal. Sci*, 18, P.167-169, (2002).
- [37] N. Babla, S. K. Bansal, and R.S. Sindhu, *Orint J. Chem.*, 6,73, (1990).
- [38] J. Medina-Esrich, A. Sevillano-Cbeza, and M.A.M. Penella, "Spectrophotometric study of the cerium (IV)-pyrogallol red system", *Analyst*, 110, 807-810, (1985).
- [39] Vera Hollriegel, Montserrat Gonzalez-Estecha, Eiena M. Trasobares, Augusto Giussani, Uwe Oeh, Miguel Angel Herraiz, Bernhard Michalke, "Measurement of Cerium in Human Breast Milk and Blood samples", *J. of trace elements in medicine and biology*, 24, P193-199, (2010).
- [40] S. Qin, Q. Yongchao, H. Bin, X. Hongchun, and J. Zucheng, *Anal. Sci.*, 16,957, (2000).
- [41] Q. Shuai, H. Bin, Y. Qin, W. Ruth, and Z. Jiang, *J. Anal. At. Spectrochem.*, 15,1413, (2000).
- [42] H.R. Pouretedal, A. Semnani and M.H. Keshararz, *Turk J.Chem.*, 30, P.711-721, (2006).
- [43] H.A. Zamani, M.R. Ganjali and M. Adib, *Sensors and Actuators B Chem.*, 120,2, P.545-550, (2007).
- [44] J. Wang, P.A.M. Farias and J.S. Mahmoud, *Anal.Chim. Acta*, 171, 1, pp 215-223, (1985).
- [45] R. Yener, and A. Aycicek, *J. Fluoresc.*, 8,45, (1998).
- [46] N. Jie, J. Yang, and T. Liu, *Talanta*, 41,415, (1994).
- [47] D.N. Taha, "A novel method for determination of hydrazine via semiautomated on-line merging zone technique", *National J. of chemistry*, 14,269-278, (2004).
- [48] D.N. Taha, "New mode for spectrophotometric determination of nanogram levels of total Iron (II) and Iron (III) by flow -injection analysis merging reaction zone for the release of iodine using valve double loops for (Fe (III), I, H3O+) system", *National J. of chemistry*, 13,43-46, (2004).