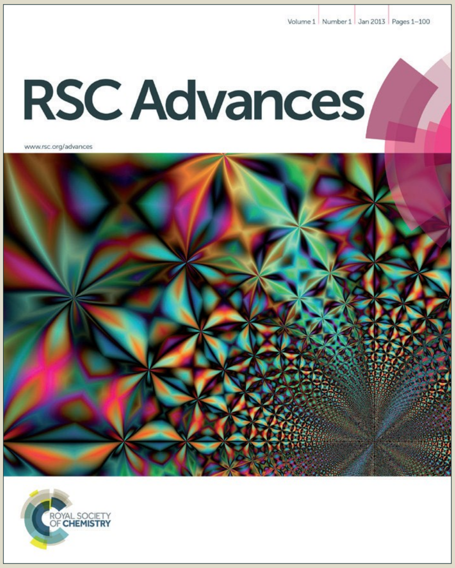
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Determination of scandium in monazite and environmental samples using cloud point extraction coupled with spectrophotometric technique

Alaa S. Amin[*,a], **Mohammed A. Kassem**[a,b] **and Sayed M.N. Moalla**[c]

[a] *Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*
[b] *Chem. Dep., Fac. of Appl. Sci., Umm Al-Qura University, Makkah, Saudi Arabia*
[c] *Chemistry Department, Faculty of Science, Port Said University, Port Said, Egypt*

A method for the determination of scandium in monazite and environmental samples at trace levels is presented. Sc(III) complex is preconcentrated with cloud point extraction process using the nonionic surfactant Triton X-100 to extract Sc(III) complex from aqueous solutions of pH 5.5. Sc(III) ion was complexed with 2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP) as a complexing agent in an aqueous medium and concentrated by Triton X-100 as a surfactant. After the phase separation at 45 °C based on the cloud point extraction of the mixture, the surfactant-rich phase was dried and the remaining phase was dissolved with 0.5 mL of dimethylformamide. Under the optimum conditions, the calibration curve is linear for the concentration range of 0.4–65 ng mL^{-1} and the detection limit was 0.12 ng mL^{-1}. The enhancement factor of 500 was achieved for 250 mL samples containing the analyte with RSDs were ≥1.10 %. The method is highly selective, fairly sensitive, simple, rapid, economical and safely applied to determine Sc(III) ion in different complex materials such as monazite and environmental samples.

Keywords: Scandium determination; Cloud point extraction; Spectrophotometry; Azo dyes; Environmental analysis

---

[*] Tel.: +20552350996; Fax: +20133222578; e-mail: asamin2005@hotmail.com

Introduction

Scandium has become an ever more important metal in sophisticated applications and high technology fields. The scarcity of scandium makes it a very expensive metal. The growing demand of scandium is due to its important application in nuclear technology, electronic component, metallurgical industry,[1] alloys, laser glass,[2,3] catalysis,[4] high-intensity metal halide lamps, and solid oxide fuel cells.

Scandium is found in nature with lanthanides and yttrium, because of their similar physicochemical properties, so it cannot easily recovered and separated.[5] In addition, the determination of Sc(III) ion in geological materials has received considerable attention in recent years because of their importance for characterizing magma sources.[6] Also, the low level of the scandium concentration in different matrices makes its direct determination by instrumental techniques difficult.

Various sensitive analytical methods such as spectrometric techniques including atomic absorption spectrometry (ICP-AAS),[7] inductively coupled plasma-mass spectrometry (ICP-MS),[8] and inductively coupled plasma atomic emission spectrometry (ICP-AES)[9-11] have been used to determine Sc(III) ion in environmental samples. Neutron activation analysis (INAA)[12-15] is often applied to the Sc(III) determination, but it requires sophisticated instrumentation that may not be available in most analytical laboratories.[16] ICP-MS has the detection power to determine trace amount of Sc(III) ion at sub-μg L^{-1} levels but it suffers from the problem of isobaric polyatomic interferences and also it is very expensive and its maintenance is so difficult.[17] In comparison, ICP-AES is a time saving, simple, and well-available method to determine Sc(III) ion in real samples.[12] However, its detection capability is still insufficient when the concentrations of Sc(III) ion are too small. Therefore, separation/ preconcentration step is required.

Many methods have been illustrated for separation/preconcentration of Sc(III) ion including ion exchange,[18] extraction chromatography,[19] solvent extraction,[20-22] flotation, electrophoresis,[23] and liquid membrane separation.[24] SPE is the most popular of all these methods, because of its advantages of high recovery, rapid phase separation, low cost, high enrichment factor, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode.[25-28]

The use of surfactants provides a lot of possibilities.[29,30] Preconcentration and separation based on the cloud point extraction emerges as an important practical technique. Most of non-ionic surfactants in aqueous solutions possess the ability to decrease their solubility rapidly and become turbid when they are heated above a temperature called the cloud point temperature (t_c).[31] For higher temperatures (above t_c) two distinct phases are formed; one containing a small portion equal to the critical micellar concentration (cmc) and the other consisting of almost the entire surfactant.[32] The mechanism of separation is attributed to the fast increase in the aggregation number of the surfactant's micelles due to an increase in the temperature.[33] The surfactant micelles have proved to entrap several hydrophobic substances, isolating them from the bulk aqueous solution during their formation,.[33,34] The centrifugation and decantation can easily separate the two phases. The species that can interact with micellar systems either directly or after being derivatized, become concentrated in a small volume of the surfactant-rich phase that can subsequently be analyzed using analytical methods such as ICP, GC, HPLC, AAS, ETAAS, CE and spectrophotometry.[35–39]

The cloud point extraction combined with spectrophotometric analysis has been used for trace metal ions determination such as Zn, Cd, Cu, Ni,[40] U,[41] Er,[42] Gd,[43] Al,[44] and Co.[45] The spectrophotometric method is limited used in Sc(III) ion analysis due to low sensitivity. However, various new highly specific and selective organic compounds are being synthesized and many highly sensitive methods is developed, increasing the applicability of these procedures.[46–61]

The aim of the present work is to combine cloud point extraction with spectrophotometric method for determination of Sc(III) ion, as a high sensitive method. This combination is favorable because spectrophotometric method is a suitable method for low volume of the remained phase obtained after CPE and for organic solvents used to dissolve the remaining analyte phase. In this work, a cloud point extraction before spectrophotometric method was used in order to determine Sc(III) ion for the first time.

Experimental

Apparatus

A water bath with good temperature control and a centrifuge with 25-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A Perkin-Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 5.0 mm quartz cell.

Reagents

Unless otherwise stated, all water is double distilled and all reagents used were of analytical and spectral purity. Standard Sc(III) ion solution (100 µg mL^{-1}) was prepared from scandium oxide, Sc_2O_3 (Specpure) (0.077 g), by dissolving in 10 mL of 6.0 mol L^{-1} hydrochloric acid and the solution was evaporated to remove the excess of acid. The salts were dissolved and diluted to 500 mL with 5.0 % (v/v) hydrochloric acid. A working solution was prepared by diluting this solution with distilled water. Working solutions were obtained by suitable dilution of the stock solution with deionized-distilled water. The surfactant, Triton X-100 (Sigma company) solution (5.0 %, v/v) was prepared by dissolving Triton X-100 with water. The materials and vessels used for the trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with doubly distilled water. The solutions of different pH 2.5–12.0 thiel buffer were prepared as described early.[62] Dimethyformamide (DMF) solvent and potassium chloride salt were purchased from Merck.

2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP) is prepared by the common way used for preparing azo dye derivative of aromatic amine.[63] 0.01 mole of *m*-toludene was converted to the hydrochloric form by adding the least amount of 1:1 HCl then diluting with water and cooling at –2.0 °C. A cooled solution of $NaNO_2$ (0.01 mole) is added gradually with continuous stirring to the amine salt. The resulting diazonium salt solution is allowed to stand in ice bath for 15 min with stirring at –2.0 °C and added gradually to a solution of 0.01 mole of 2-amino-3-hydroxypyridine dissolved in 10% NaOH which cooled at –2.0 °C. The resulting solution is allowed to stand for 15 min with constant stirring until the azo dye completely formed. The obtained azo is filtered off, dried and recrystallized in ethanol. The purity of the resulting azo dye is checked by measuring the melting point constancy. The chemical structure is detected by melting point, elemental analysis (C, H, N), IR and ^{1}H-NMR spectra. The separated azo has the structural formula as shown in (Scheme 1).

A 5×10^{-3} mol L^{-1} solution of the reagent was prepared by dissolving an appropriate weight of reagent in 10 mL ethanol and then completed to the mark in 100 mL calibrated flask.

General procedure

An aliquot of 100 µg mL^{-1} Sc(III) ion standard solution was transferred to a 250 mL measuring flask, 8.0 mL of the 5×10^{-3} mol L^{-1} ATAP solution and 30 mL buffer solution of pH 5.5 were added. This was followed by the addition of 10 mL of 5.0 % (v/v) Triton X-100. The solution was taken up to the mark with bidistilled water. The content was warmed at water bath of 45 ± 1.0 ^{o}C and allowed to stand for 10 min. Since the surfactant density is higher than water, the surfactant-rich phase typically settles through the aqueous phase. The separation of the phase was accelerated by centrifuging at 3800 rpm for 10 time in 25 mL tube for 5.0 min. On the cooling stage in an ice-bath, the surfactant-rich phase became viscous. Then, the aqueous phase was separated by simple decantation. Later, surfactant rich phase was heated in oven at 100 ^{o}C to remove the remaining water. 0.5 mL of DMF was added to the remaining phase and then the sample was transferred 5.0 mm quartz cell. The absorbance of the solution was measured at 636 nm. The blank solution was submitted to the same procedure with Sc(III).

Determination of Sc(III) ion in spiked and natural water samples

The extraction efficiency was studied using spiked water samples for the recovery of Sc(III) ion. Doubly distilled water was spiked with known amounts of Sc(III) standards (20, 40 and 60 ng mL^{-1}) and allowed to stand over night. The concentration of Sc(III) ion in spiked water samples was determined. The natural water samples filtered through a 0.45 µm pore size membrane filter to remove suspended particulate matter and then stored at 4.0 ^{o}C in the dark. The final solution was determined by following the above general procedure.

Analysis of a monazite sand sample

A 2.0 g of the sample was completely dissolved in a minimum volume of concentrated sulfuric acid (about 20 mL) by heating on a water bath. The solution was evaporated to near dryness. To this a small volume of water was added and neutralized with sodium hydroxide. The solution was cooled, filtered and diluted to 100 mL (0.1 mol L^{-1} HCl).

Determination of Sc(III) ion in alloys

To an appropriate amount of sample, add 10 mL of (1 + 1) aqua regia, heat to decompose the sample and evaporate to near dryness. After cooling to room temperature, dissolve the residue with water and neutralized with sodium hydroxide, transfer the solution to a 100-mL calibrated flask and dilute to the mark with water. Place an aliquot part of the resultant solution in a 100-mL beaker, add 1 mL of 5.0% (w/v) ascorbic acid solution, then follow the general procedure for the determination of Sc(III) ion.

Results and discussion

In solution, ATAP showed maximum absorbance at 517 (pH 5.5) and 496 nm (pH 8.5). It reacts with Sc(III) at pH values 5.5, to form violet complex having a maximum absorbance at 614 nm. The addition of surfactant-active substances improves the selectivity and sensitivity of Sc(III) determinations due to the batho- and hyperchromic effects that can be observed. The absorption bands of ATAP and its complex in DMF medium after separation of surfactant-rich phase are located at 529 and at 636 nm, respectively [Fig. 1].

Optimization of the system

To take full advantage of the procedure, the reagent and surfactant concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to achieve optimum conditions. These parameters were optimized by setting all parameters to be constant and optimizing one each time.

The effect of pH on the absorbance at a constant concentration of complex in surfactant-rich phase was investigated in the range of 2.5–12.0. Various types of buffers (acetate, borate, phosphate, thiel, and universal) were examined and the results showed that the optimum one is thiel buffer solutions. The absorbance of the Sc(III)–ATAP–Triton X-100 system at 636 nm in surfactant-rich phase was studied against ATAP as blank. The absorbance was nearly constant in the pH range of 5.0–6.0. Therefore, pH 5.5 was selected as optimal [Fig. 2]. Moreover, the amount of pH 5.5 was studied to select the optimum volume. A 25–35 mL of pH 5.5 gave the highest absorbance value. Therefore 30 mL of pH 5.5 was selected for all further studies in a measuring flask of 250 mL.

Effect of ATAP concentration on the extraction and determination of Sc(III) was investigated in the range of 1.0 –14 × 10^{-5} mol L^{-1}. The sensitivity of the method increased by increasing ATAP concentration up to 8 × 10^{-5} mol L^{-1} and decreased at higher concentrations. It was expected that increasing ATAP causes an increase in the absorbance of complex, because increasing in ATAP concentration caused an increase in concentration of the complex. At concentrations higher than 10 × 10^{-5} mol L^{-1}, the concentration of uncomplexed ATAP in surfactant-rich phase increases significantly. Therefore, much probably decrease of absorbance change at concentrations higher than 10 × 10^{-5} mol L^{-1} is due to this fact that the free ATAP competes with the complexes in extraction to surfactant-rich phase. A concentration of 8 × 10^{-5} mol L^{-1} of ATAP was selected as the optimum.

The effects of surfactants on the Sc(III)–ATAP system were investigated. The results showed that, in the absence and presence of anionic or cationic surfactants, the Sc(III)–ATAP chromogenic system gives a low absorption, whereas in the presence of nonionic surfactants, the absorption of the chromogenic system increases markedly. Various nonionic surfactants enhance the absorbance in the following sequence: Triton X-100 > emulsifier-OP > Triton X-114 > Tween-80 > Tween-60 > Tween-20. Effect of Triton X-100 concentration on the extraction and determination of Sc(III) was investigated in the range of 1.0–8.0 mL of 5.0 % Triton X-100. The amount of the absorbance for sample increased by increasing Triton X-100 concentration up to 10 mL of 5.0 % (v/v), and decreased at higher concentrations. The blank absorbance also increased by increasing Triton X-100 concentration. This is due to more extraction of ATAP by increasing Triton X-100 concentration, but the difference between the sample and blank (ΔA) increased by increasing Triton X-100 concentration up to10 mL of 5.0 % (v/v) Triton X-100 and decreased at higher concentrations (Fig. 3). Therefore, 10 mL of 5.0 % (v/v) Triton X-100 was chosen as the optimum.

It is suitable to choose the shortest equilibration time and the lowest possible equilibration temperature which ensures completion of phase separation in the cloud point extraction. An excellent absorbance was obtained for the equilibration temperature from 40 to 50 ^{o}C. Therefore, temperature of 45 ^{o}C was used in subsequent experiments (Fig. 4). The dependence of absorbance upon incubation time was studied in the range of 5.0–15 min and the optimum time of 10 min was chosen as a suitable time. Also a 5.0 min centrifugation at 3800 rpm was found to be enough for successful CPE.

Because the surfactant-rich phase was precipitate, different solvents were tried so as to select the one producing the optimal results regarding sensitivity. Among methanol, ethanol, DMF, acetonitrile, acetone and dioxane, DMF gave the best results due to high sensitivity and low overlapping of spectra of components. Therefore, DMF was chosen in order to have appropriate amount of sample for transferring and measurement of the absorbance of the sample and also a suitable preconcentration factor. The amount of 0.5 mL DMF was chosen to have an appropriate amount of sample for transferring and measuring the absorbance. Therefore, a preconcentration factor of 500 was archived using the proposed method.

Stoichiometric ratio

The nature of the complex was established at the optimum conditions described above using the continuous variation and molar ratio methods. the Job method showed a ratio of ATAP to Sc(III) = 3.0. Moreover, The plot of absorbance versus the molar ratio of ATAP to Sc(III), obtained by varying the ATAP concentration, showed inflection at molar ratio 3.0, indicating presence of three ATAP molecules in the formed complex. Consequently, the results indicated that the stoichiometric ratio was (3:1) [ATAP : Sc(III)]. The conditional formation constant (log K), calculated using Harvey and Manning equation applying the data obtained from the above two methods, using the following equation[64,65] was found to be 5.46, whereas the true constant was 5.37.

$$K_f = \frac{A/Am}{[1\text{-}\ A/Am]^{n+2}\ C_M\ (n)^{\mathrm{n}}}$$

where A is the observed maximum absorbance, A_m is the absorbance value corresponding to intersection of the two tangents of the curve, C_M is the mole concentration corresponding to maximum absorbance, and n is the stoichiometry with which reagent complex with Sc(III).

Selectivity

Without CPE there are many interferences from different cations and anions. Considering the selectivity provided by the cloud point extraction and spectrophotometric determination, many anions and cations were examined. An ion was considered to interfere when its presence produced a variation of ± 5.0% in absorbance of sample. In these experiments, solutions containing 40 ng mL^{-1} of Sc(III) and interfering ions were treated according to the batch procedure. The results represented in Table 1 showed that up to 6.0 μg mL^{-1} of Y^{3+}, La^{3+}, Ce^{3+}, Dy^{3+}, Er^{3+}, Eu^{3+}, Ho^{3+}, Y^{3+}, 1500 μg mL^{-1} of Ca^{2+}, Na^{+}, K^{+}, Mg^{2+} and 75 μg mL^{-1}

of Pb^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Cu^{2+} ions did not interfere with the determination of Sc(III). The recoveries of Sc(III) were not less than those in the absence of coexisting ions, indicating that ATAP had a high selectivity towards Sc(III) and have a potential to be applied to analyze real sample.

Analytical characteristics

Table 2 summarizes the analytical characteristics of the optimized method, including regression equation, linear range and limit of detection, reproducibility, and enhancement factors. The limit of detection,[66] defined as $C_L = 3S_B/m$ (where C_L, S_B, and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.12 ng mL^{-1}. Because the amount of Sc(III) in 250 mL of sample solution is measured after preconcentration in a final volume of 0.5 mL DMF, the solution is concentrated by an enhancement factor of 500. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that of the calibration graph in micellar media without preconcentration, was 1141.

The relative standard deviation (RSD) and relative error for six replicate measurements of 40 ng mL^{-1} of Sc(III) was 1.10% and 1.56% and for 75 ng mL^{-1} was 1.15% and 1.67%, respectively.

Several methods have been reported for the determination of scandium in various types of samples such as solvent extraction, extraction chromatography, ion exchange, chemical precipitation, flotation, electrophoresis, and liquid membrane separation[9,15,16,25-27] as well as their combined techniques.[4] However, these methods are complicated, time-consuming and/or reagent-consuming, sensitivity lowly, costs highly and the scandium yield of those methods is low.[4,10] In compared with those methods mentioned above, the present method possessed the advantages of excellent selectivity, short analysis time, high enrichment factor, low consumption of organic solvents and low costs. Though it takes relatively long time for preparation of the material than the reported literature,[26] it shows more mild reaction conditions. It also shows better or comparable capacity value to other solid support used for enrichment of Sc(III) mentioned above.

The sensitivity expressed as molar absorptivity of the proposed method is compared with those of published spectrophotometric methods [Table 3]. The higher sensitivity of the proposed method is notable, greater even than that all other method, that based on spectrophotometry.

Analytical applications

Aiming to demonstrate the usefulness of the proposed system a set of samples comprising several spiked water samples was analyzed. The results of sample are shown in Table 4. Accuracy was assessed by comparing results with these obtained using ICP-AES.[14] The recoveries are close to 100% and indicate the proposed method was helpful for the determination of Sc(III) in the real samples.

The performance of the proposed method was assessed by calculation of the t- value (for accuracy) and F- test (for precision)[67] compared with ICP-AES method. The results showed that the calculated values (Table 4) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method.

In order to ascertain the accuracy of the suggested procedure, the method was applied to the determinations of trace Sc(III) in fish, orange leaves, kaolin ore and monazite sand samples; which are grown in the region under study. The results were listed in Tables 5 and 6. The analytical results for fish, orange leaves, kaolin ore and monazite sand were in agreement with ICP-AES. The results indicate that the proposed method is reliable.

Synthetic samples were prepared by introducing known amounts of Sc(III) to solutions of standard samples and samples of copper, zinc, magnesium alloys and low-alloy steel, and the Sc(III) contents were determined by using the above general procedure. The results are shown in Table 7. The recoveries of Sc(III) obtained ranged from 98.76 to 101.88.

Conclusion

The present work gives a very simple, sensitive and low-cost CPE coupled with spectrophotometric method to determine Sc(III) ion that can be applied to different complex materials such as monazite and environmental samples. The surfactant is used for enrichment of Sc(III) ions in water, and thus toxic solvent extraction, has been avoided. A comparison between the present method with the previously investigated spectrophotometric methods for Sc(III) ion determination shows that the present method has safe, simple, a lower linear range, higher sensitivity, and is a convenient, fast and inexpensive method for the determination of trace microamounts of Sc(III) ion to monazite and environmental samples.

References

1 J. Gambogi, "*Mineral Commodity Summaries, Scandium*", 2014, U.S. Geological Survey, 140.

2 M. Ochsentihn-Petropulu, T. Lyberopulu and G. Parissakis, *Anal. Chim. Acta* 1995, **315**, 231.

3 D. Mohr, A.S.S. de Camargo, C.C. de Araujo, and H. Eckert, *J. Mater. Chem.* 2007, **17,** 3733.

4 B.Y. Park, K.Y. Ryu, J.H. Park, and S. Lee, *Green Chem.* 2009, **7,** 946.

5 X. Sun, Y. Ji, L. Guo, J. Chen, and D. Li, *Sep. Purif. Tech.* 2011, **81**, 25.

6 N. Lihareva and M. Delaloye, *Fresenius J. Anal. Chem.* 1997*,* **357***,* 314.

7 J.G.S. Gupta, *Talanta* 1984*,* **31***,* 1045.

8 W.R. Pedreira, C.A. Queiroz, A. Abrao, S.M. Rocha, M.E. de Vasconcellos, G.R. Boaventura and M.M. Pimentel, *J. Alloys Compd.* 2006*,* **418**, 247.

9 J. Jerez, A.C. Isaguirre and C. Bazán, *Talanta* 2014*,* **124***,* 89.

10 G.V. Ramanaiah, *Talanta* 1998*,* **46**, 533.

11 K. Satyanarayana, S. Durani and G.V. Ramanaiah, *Anal. Chim. Acta* 1998**, 376**, 273.

12 M. Nomura, M. Sato, H. Amakawa, Y. Oura and M. Ebihara, *Anal. Chim. Acta* 2005, **553***,* 58.

13 B.J.B. Nyarko, E.H.K. Akaho, J.J. Fletcher and A. Chatt, *Appl. Radiat. Isotopes* 2008*,* **66**, 1067.

14 K. Satyanarayana, S. Durani and G.V. Ramanaiah, *Anal. Chim. Acta* 1998*,* **376***,* 273.

15 L.J. Zhang, X.J. Chang, Y.H. Zhai, Q. He, X.P. Huang, Z. Hu and N. Jiang, *Anal. Chim. Acta* 2008*,* **629**, 84.

16 S. Cerutti, J.A. Salonia, J.A. Gasquez, R.A. Olsina and L.D. Martinez, *J. Anal. Atom. Spectrom.* 2003*,* **18***,* 1198.

17 S. Hirata, T. Kajiya, M. Aihara, K. Honda and D.Shikino, *Talanta* 2002*,* **58**, 1185.

18 G. Guo and Y. Chen, *Hydrometallurgy* 1990*,* **23**, 333.

19 H. Minowa and M. Ebihara, *Anal. Chim. Acta* 2003*,* **498***,* 25.

20 M. Karve and B.Vaidya, *Sep. Sci. Technol.* 2008*,* **43***,* 1111.

21 D. Wu, C. Niu, D. Li and Y. Bai, *J. Alloys Compd.* 2004*,* **374***,* 442.

22 M. Karve and B. Vaidya, *Indian J. Chem. (A)* 2006*,* **45**, 2658.

23 S. Himeno, E. Kitano, M. Kanaya and M. Takamoto, *Talanta* 2007*,* **71**, 822.

24 X. Yang, Z. Gu and D. Wang, *J. Membr. Sci.* 1995*,* **106** , 131.

25 K. Pyrzynska and M. Trojanowicz, *Crit. Rev. Anal. Chem.* 1999*,* **29***,* 313.

26 Q. He, X. Chang, Q. Wu, X. Huang, Z. Hu and Y. Zhai, *Anal. Chim. Acta* 2007**, 605***,* 192.

27 M.H. Chhatre and V.M. Shinde, *Talanta* 1998*,* **47***,* 413.

28 M. Kooshki and E. Shams, *Anal. Chim. Acta* 2007*,* **587***,* 110.

29 Q. Fang, M. Du and C.W. Huie, *Anal. Chem.* 2001*,* **73**, 3502.

30 J.L. Manzoori and A.Bavili-Tabrizi, *Microchem. J.* 2002*,* **72***,* 1.

31 B.M. Cordero, J.L.P. Pavon, C.G. Pinto and E.F. Laespada, *Talanta* 1993*,* **40***,* 1703.

32 M.J. Schick, (Ed.), *Non-ionic Surfactants,* Marcel Dekker, New York, 1987.

33 M.J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1987.

34 F. Xia and R.M. Cassidy, *Anal. Chem.* 1991*,* **3,** 2883.

35 H.İ. Ulusoy, R. Gürkan, Ö. Yılmaz and M. Akçay, *J. Anal. Chem.,* 2012, **67,** 131.

36 H.İ. Ulusoy, Ü. Aksoy and M. Akçay, *Eur. Food Res.& Tech.* 2013, **236**, 725.

37 H.İ. Ulusoy, *J. AOAC Inter.* 2014, **97***,* 238.

38 H.İ. Ulusoy, *J. Radioanal. & Nucl. Chem.* 2014, **302**, 497**.**

39 H.İ. Ulusoy, R. Gürkan, Ö. Demir and S. Ulusoy, *Food Anal. Methods,* 2012, **5***,* 454.

40 H. Watanabe, T. Saitoh, T. Kamidate and K. Haraguchi, *Mikrochim. Acta* 1992*,* **106***,* 83.

41 F. Shemirani, R.R. Kozani, M.R. Jamali, Y. Asadi anf M.R. Milani, *Sep. Sci. Technol.* 2005*,* **40***,* 2527.

42 M.F. Silva, L.P. Fernandez, R.A. Olsina and D. Stacchiola, *Anal. Chim. Acta* 1997*,* **342***,* 229.

43 M.F. Silva, L.P. Fernandez and R.A. Olsina, *Analyst* 1998**, 123**, 1803.

44 L. Sombra, M. Luconi, M.F. Silva, R.A. Olsina and L.P. Fernandez, *Analyst* 2001*,* **126**, 1172.

45 A. Safavi, H. Abdollahi, M.R.H. Nezhad and R. Kamali, *Spectrochim. Acta A* 2004, **60**, 2897.

46 S.S. Berman, G. R. Duval and D.S. Russell, Anal. Chem. 1963*,* **35***,* 1392.

47 S.B. Savvin, *Talanta* 1961*, **8,*** 673.

48 C. Vekhande and K.N. Munshi, *Microchem. J.* 1978*,* **23***,* 28.

49 M. Jarosz and Z. Marczenko, *Anal. Chim. Acta* 1984*,* **159**, 309.

50 W.R. Chen, J.M. Pan, C.G. Hsu and S.S. Ge, *Mikrochim. Acta* 1985*,* **III***,* 417.

51 C. Park and K. Cha, *Korean Chem. Soc.* 1999**, 20***,* 1409.

52 C.-G. Hsu, Q. Xu and J.-M. Pan, *Mikrochim. Acta* 1997*,* **126***,* 83.

53 Z. Li, J. Wang and Q. Xu, *Anal. Sci.* 1996**, 12***,* 259.

54 P.W. Beaupre and W.J. Holland, *Mikrochim. Acta [Wien]* 1982*,* **II***,* 419.

55 H. Onishi and C.V. Banks, *Anal. Chim. Acta* 1963*,* **29**, 240.

56 V.A. Nazarenko and V.P. Antonovitch, *Zh. Analit. Khim.* 1969*,* **24***,* 1008.

57 V. I. Fadeeva and I. P. Alimarin, *Zh. Analit. Khim.* 1962*,* **17**, 1020.

58 T. Shimizu, *Talanta* 1967*,* **14***,* 473.

59 T. Shimizu and E. Momo, *Anal. Chim. Acta* 1970*,* **52**, 146.

60 K. Uesugi, *Anal. Chim. Acta* 1970, **49***,* 597.

61 L.A. Sarsam and W.A. Bashir, *J. Raf. Sci.,* 2009*,* **20***,* 48.

62 H.T.S. Britton "*Hydrogen Ions*", 4th edn., Chapman and Hall, London, 1952.

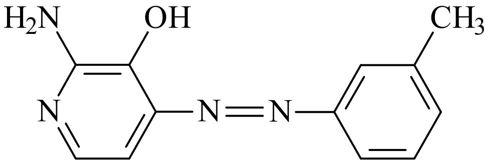
63 A.S. Amin, M.A. Kassem, and T.Y. Mohammed, *RCS Advances,* 2015**, 5**, 25095.

64 J. Davidge, C.P. Thomas and D.R. Williams, *Chem. Spec. & Bioavail.* 2001, **13**, 129.

65 International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use, ICH Harmonized Tripartite Guideline, *Validation of Analytical Procedures: Text and Methodology*, Q2(R1), 2005. Complementary Guideline on Methodology dated 06 November, ICH, London, UK, 1996.

66 IUPAC, *Spectrochim. Acta B* 1978*,* **33***,* 241.

67 J.N. Miller and J.C. Miller, "*Statistics and Chemometrics for Analytical Chemistry"* 5th ed., Prentice Hall, England, 2005.



Scheme 1. 2-amino-4-(m-tolyazo)pyridine-3-ol (ATAP)

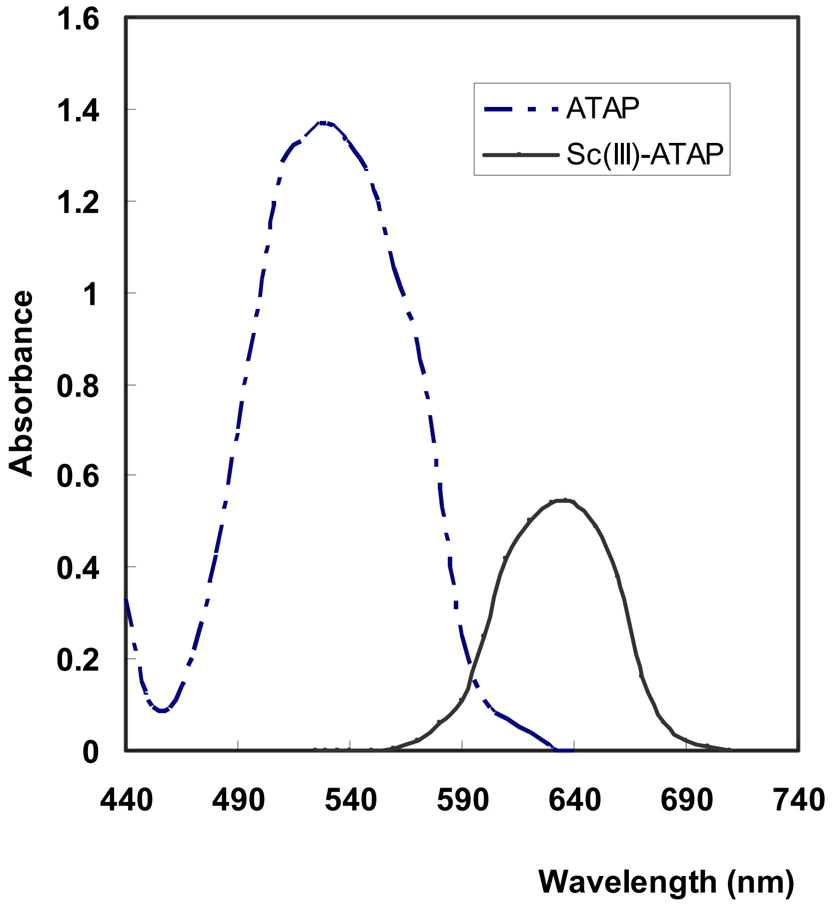


Figure 1. Aborption spectra for 8 × 10^{-5} mol L^{-1} ATAP and its complex with 40 ng mL^{-1} Sc(III) using 30 mL of pH 5.5; 10 mL of 5.0 % Triton X-100; at 45 ± 1.0 °C; separation centrifuging at 3800 rpm; heated at 100 °C and then dissolved in 0.5 mL of DMF

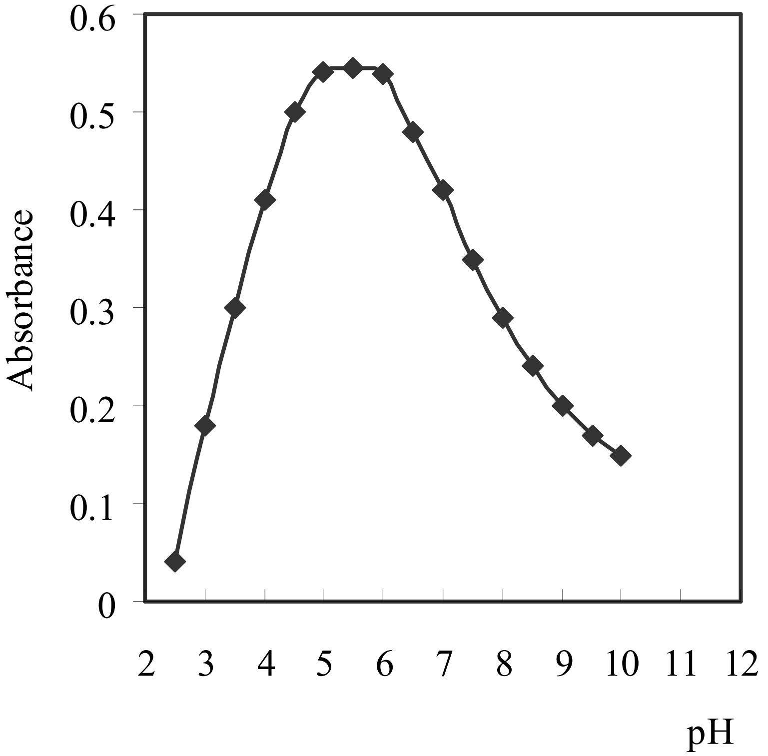


Figure 2. Effect of pH on the complexation of 40 ng mL^{-1} of Sc(III) with 8 x 10^{-5} mol L^{-1} ATAP using 30 mL of pH 5.5; 10 mL of 5.0 % Triton X-100; at 45 ± 1.0 °C; centrifuging at 3800 rpm; heated at 100 °C and then dissolved in 0.5 mL of DMF

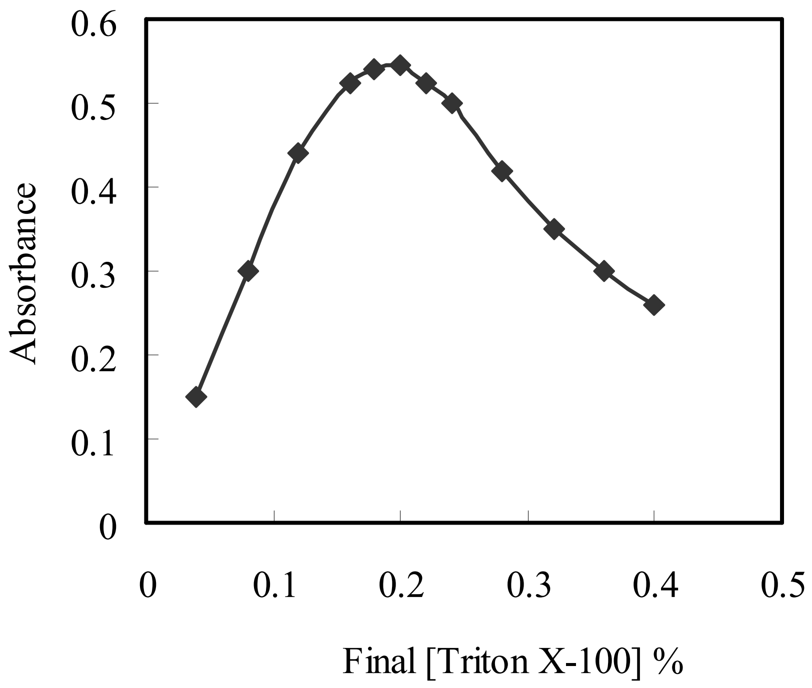


Figure 3. Effect of Triton X-100 % on the complexation of 40 ng mL^{-1} Sc(III) with 8 x 10^{-5} mol L^{-1} ATAP using 30 mL of pH 5.5; 10 mL of 5 % Triton X-100; at 45 ^{o}C; centrifuging at 3800 rpm; heated at 100 ^{o}C and then dissolved in 0.5 mL of DMF

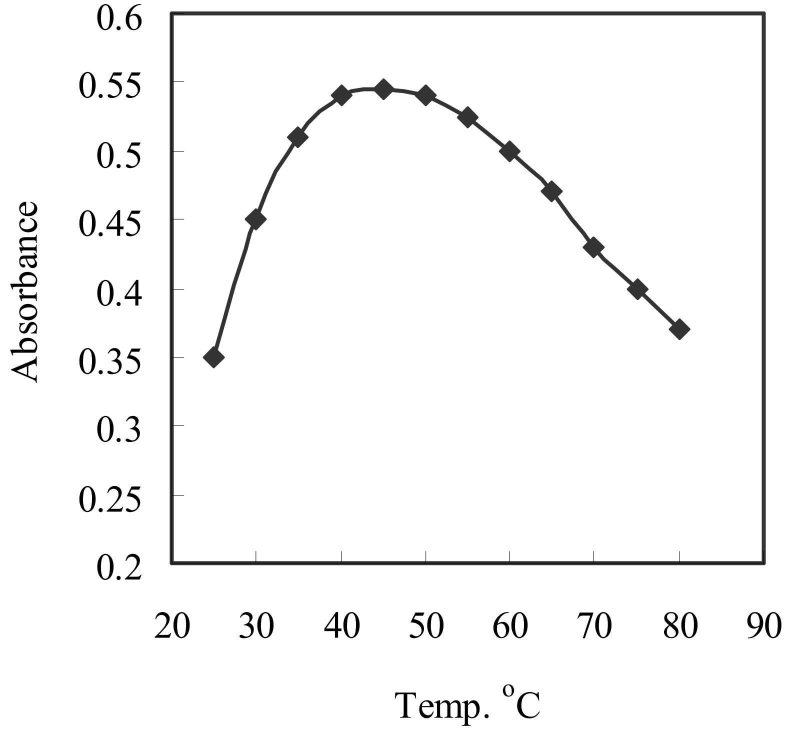


Figure 4. Effect of temperature on the phase separation of 40 ng mL^{-1} Sc(III) complexed with 8 x 10^{-5} mol L^{-1} ATAP using 30 mL of pH 5.5; 10 mL of 5 % Triton X-100; at 45 °C; centrifuging at 3800 rpm; heated at 100 °C and then dissolved in 0.5 mL of DMF

Table 1 Effect of foreign ions on recovery of 40 ng mL^{-1} Sc(III) ion

Coexisting ions	Concentration (μg mL^{-1})	Recovery of Sc(III) (%)
La^{3+}	6.00	97.5
Y^{3+}	6.00	96.8
Er^{3+}	6.00	98.3
Dy^{3+}	6.00	96.1
Ce^{3+}	6.00	95.3
Eu^{3+}	6.00	97.4
Yb^{3+}	6.00	98.6
Ho^{3+}	6.00	98.5
K^{+}	1500	98.2
Na^{+}	1500	98.0
Ca^{2+}	1500	97.8
Mg^{2+}	1500	97.5
Mn^{2+}	75	97.0
Cu^{2+}	75	96.7
Cr^{3+}	75	98.5
Zn^{2+}	75	97.6
Pb^{2+}	75	99.0

Table 2 Analytical features of the proposed method

Parameters	CPE method	Before CPE
Amount of DMF	0.5	---
pH	5.5	5.5
Optimum [BTABD]	8×10^{-5}	8×10^{-5}
Reaction time (min)	10	25
Stirring time (min)	5.0	----
Beer's range (ng $mL^{-1)}$	0.4 - 65	5000 - 55000
Ringbom range (ng $mL^{-1)}$	1.0 - 62	8000 - 52500
Molar absorptivity (L mol^{-1} cm^{-1})	6.16×10^5	548
Sandell sensitivity (ng cm^{-2})	0.0073	82.5
Regression equation		
Slope (µg mL^{-1})	13.69	0.012
Intercept	0.004	-0.03
Correlation coefficient (*r*)	0.9996	0.9980
RSD [a] (%)	1.10	2.50
Detection limits (ng mL^{-1})	0.12	1500
Quantification limits (ng mL^{-1})	0.40	4950
enhancement factor	500	--
Improvement factor	1141	--

Table 3 A comparison between the figures of merits and the published methods

Reagents	λ (nm)	ε × 10^{-4} L mol^{-1} cm^{-1}	Liner range μg mL^{-1}	Ref.
Xylenol orange	560	2.9	0.5–1.7	[46]
Arzenazo III	675	1.9	2.5–25	[47]
Eriochrome azural B	650	9.85	5.0 –65	[48]
Chromazural S	610	15.0	1.3–16.2	[49]
4,5-Dibromophenylfluorone	590	22.6	0.0 – 6.0	[50]
Eriochrome cyanine R	610	56.1	2.0 – 60	[51]
p-Nitrochlorophosphonazo	689	27.6	0.3– 8.0	[52]
Nile blue	585	35.9	0.8 – 40	[53]
Disodium 3-hydroxy-4-[(6-methyl-2-pyridyl)azo]-2,7-naphthalene disulfonate N-oxide	555	1.55	2.0 – 26	[54]
Arsenazo I	570	1.70	0.5 – 55	[55]
Arsenazo M	664	2.85	2.5– 95	[56]
Chlorophosphonazo lII	690	1.25	1.0 – 32	[57]
Bromopyrogallol Red	610	2.4	0.5 – 45	[58]
4-(2-Thiazolylazo)-resorcinol (TAR)	540	5.06	5.0–100	[59]
Eriochrome Brilliant Violet B	562	2.4	1.0–15	[60]
Eriochrome Cyanine R and cetylpyridinium Chloride	595	13	0.2–12.5	[61]
ATAP-Triton X-100-CPE	636	61.6	>0.065	This work

Table 4 Recovery of Sc(III) ion from spiked water samples using the proposed method.

Sample	Proposed method (concentration added)					
	20 ng mL^{-1}		40 ng mL^{-1}		60 ng mL^{-1}	
	Found	Recovery (%)[a]	Found	Recovery (%)[a]	Found	Recovery (%)[a]
Tap water-I[b]	20.1	100.50 ± 0.32	40.3	100.75 ± 0.28	60.2	100.33 ± 0.43
t- and *f*-test		0.96 and 2.08		0.76 and 1.83		1.16 and 2.43
	ICP-AES method (concentration added) [14]					
	19.9	99.50 ± 1.75	39.6	99.00 ± 0.87	60.5	10083± 0.96
River water-I[c]	19.8	99.00 ± 0.88	40.2	100.50 ± 1.25	59.8	99.67 ± 0.79
t- and *f*-test		0. 76 and 1.73		1.21 and 2.56		0.81 and 1.77
	ICP-AES method (concentration added) [14]					
	19.7	98.50 ± 0.92	40.4	101.00 ± 1.56	59.5	99.17 ± 1.69
Sea water- I[d]	20.25	101.25 ± 0.79	39.8	99.50 ± 0.97	59.9	99.83 ± 0.69
t- and *f*-test		1.17 and 2.58		0.95 and 2.09		0.82 and 2.16
	ICP-AES method (concentration added) [14]					
	20.3	101.50 ± 1.11	40.5	101.25 ± 0.76	60.3	100.50 ± 0.90
Well water- I[e]	20.1	100.50 ± 0.72	39.9	99.75 ± 0.78	60.1	100.17 ± 0.57
t- and *f*-test		0.91 and 2.05		0.79 and 1.92		0.73 and 1.67
	ICP-AES method (concentration added) [14]					
	20.3	101.50 ± 1.36	39.8	99.50 ± 1.57	59.6	99.33 ± 1.59
Wastewater-I[b]	20.0	100.00 ± 0.56	40.1	100.25 ± 0.95	60.2	100.33 ± 1.13
t- and *f*-test		1.22 and 2.67		1.11 and 2.44		1.08 and 2.36
	ICP-AES method (concentration added) [14]					
	20.2	101.00 ± 1.43	39.7	99.25 ± 1.63	59.6	99.33 ± 1.37

[a] Mean ± S.D. (n = 6).

[b] Collected from Benha, Egypt. [c] Collected from Shoubra, Egypt.

[d] Collected from Alexandria, Egypt [e] Collected from Zagazig, Egypt.

Table 5 Analytical results to determine Sc(III) in environmental samples.

Sample	Concentration of Sc(III) (μg g^{-1})				
	Added	Found[a] by this method	Recovery (%)	Found[a] by ICP-AES	Recovery (%)
Fish	0	0.17± 0.04	--	0.17 ± 0.10	--
	0.5	0.66± 0.11	98.5	0.65 ± 0.17	97.01
	1.0	1.18± 0.13	100.85	1.19± 0.33	101.17
Orange leaves	0	–		–	
	0.5	0.49 ± 0.02	98.0	0.48 ± 0.11	96.0
	1.0	1.01 ± 0.08	101.0	0.98 ± 0.32	98.0
Soil sample	0	0.20 ± 0.03	--	0.19 ± 0.26	--
	0.5	0.71 ± 0.16	101.43	0.67 ± 0.44	97.1
	1.0	1.19 ± 0.22	99.17	1.16 ± 0.23	97.5
Balsam pear leaves	0	0.21	--	0.20	--
	0.5	0.70	98.59	0.71	101.43
	1.0	1.23	101.65	1.16	96.67
Lotus leaves	0	–		–	
	0.5	0.5	100	0.51	102.00
	1.0	0.99	99.00	0.97	0.98

–: not detected.

[a] The value following "±" is the standard deviation (n = 6).

Table 6 The results of Sc(III) spiked monazite digest solution analysis.

Sc^{3+} spiked	Sc^{3+} Found (ng mL^{-1})		Recovery (%)	
(ng mL^{-1})	Proposed	ICP-AES	Proposed	ICP-AES
0	42	42.2	--	--
4.0	46.1	46.0	100.22	99.57
8.0	49.9	50.5	99.80	100.60
12.0	54.2	53.8	100.37	99.26
16.0	58.2	57.7	100.34	99.14
20.0	61.8	62.6	99.68	100.64

matrix composition (mg/100 mL): Ce(IV); 310, La(III); 231, Pr(III); 4, Nd(III); 9, Sm(III); 0.3, Y(III); 8.

Table 7 Determination of scandium in alloys

Sample [a]	Scandium (10^{-3} %)		Coefficient of variation(%)	Recovery (%)
	Content	Found[b]		
Aluminum-brass (BY1912-1)	2.42	2.39	2.78	98.76
Manganese-brass (BY1914-1)	3.20	3.26	3.45	101.88
Zinc alloy (47 #)	3.11	3.15	2.88	101.29
Low-alloy steel (31-5)	2.41	2.37	4.14	98.34
Magnesium alloy (ZMs)	3.90	3.92	2.09	100.51

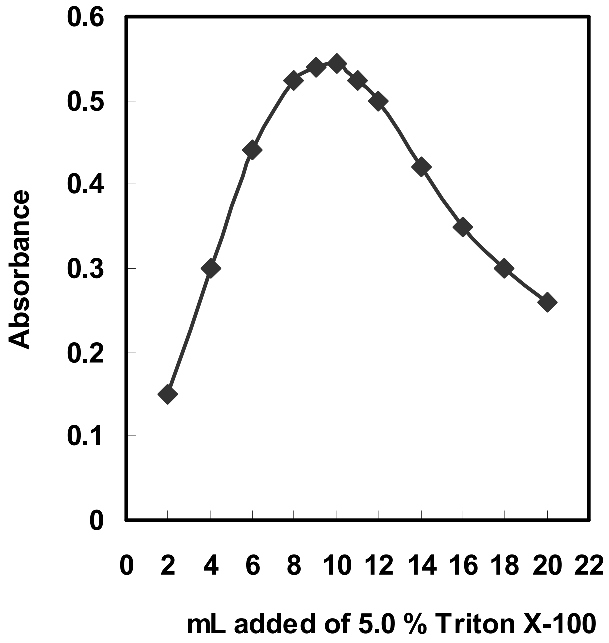
[a] Compositions of standard samples (%):

Aluminum-brass BY1912-1: Cu(57.66), A1(3.46), Ni(2.50), Fe(0.43), Pb(0.076), Bi(0.0023), Sb(0.0040) P(0.0080).

Manganese-brass BY1914-1: Cu(57.09), Mn(3.23), Al(1.18), Fe(0.98), Pb(0.18), Bi(0.0017), Sb(0.0044), P(0.013).

Low-alloy steel 31-5: C(0.087), Si(0.360), Mn(1.033), P(0.0123), Cr(0.033), Ni(0.350), V(0.231), Mo(0.152), Ti(0.150), Cu(0.435), Al(0.106).

[b] Mean of six determinations.



Effect of 5.0 % Triton X-100 on the complexation of 40 ng mL^{-1} Sc(III) with ATAP