Asian Journal of Chemistry Vol. 21, No. 5 (2009), 4013-4016

Determination of Trace Amounts of Aniline in Mixed Water-Ethanol Solution by Coulometric Titration

A.M. ATTARAN*, H. PARHAM† and M. RAEISZADEH†
Department of Chemistry, Payame Noor University, Tehran, Iran
E-mail: m_ataran@pnu.ac.ir; a_m_attaran@yahoo.com

A sensitive and simple constant current coulometric method is introduced for determination of aniline in the presence of sulfite (major interfering substance) in mixed water:ethanol (80:20) solution. Formaldehyde or acetaldehyde can mask the sulfite component. Measurement of coulometric time of the analyte in the solution mixture in which sulfite is masked by formaldehyde can be used to determine the concentrations of aniline. Relative standard deviations (RSD) of all measurements lie in the range of 0.1- 2.1 %. The effect of different parameters such as pH, concentration of reagents, salt concentration and effect of interferences are studied. The proposed method can determine 1.0×10^{-7} moles of aniline in the presence of large amounts of sulfite masked by formaldehyde. The current efficiency of the method is estimated to be ≥ 98.5 %. The proposed method can be used for the determination of aniline in the presence of real sample matrixes (such as tap water) with good accuracy and precision.

Key Words: Coulometric titration, Aniline, Formaldehyde.

INTRODUCTION

The use of electrochemical methods in trace analysis is well documented. Their role and importance especially in routine analysis have been improved in recent decades due to the advent of powerful computerized electroanalytical techniques. Coulometric titration using electrogenerated I_2 and Br_2 has been used long in the determination of different organic and inorganic substances and also bromation of some drug compounds[1-7]. This approach allows more precise analytical results than the usual bromimetric titration owing to Br_2 electrogeneration directly in the coulometric cell and better control over the regeneration rate. Moreover, the determination is rapid because no titrant preparation, standardization and storage are required. Also the possibility of carrying out a few successive titrations without changing the supporting electrolyte and the simplicity of calculating the amount of the analyte is achieved.

A major weakness, common to titrimetric methods is the lack of selectivity and also analyte detection[8]. Simultaneous determination of analytes and finding

---

†Research & Science Center, Islamic Azad University, Ahvaz, Iran.

more sensitive methods of end-point detection remain an active research area in coulometric titrations[9-13]. Computers and electronics played an increasing role in this effort[14].

The present paper aims to explore a new method for determination of aniline, in aqueous-non-aqueous media in the presence of a major interfering component, sulfite ion. The end point of titration was followed by colour change of methyl red indicator from red to colourless at pH = 4.

EXPERIMENTAL

Measurements were carried out on a JC100 model coulometer equipped with two 7 × 4 mm Pt electrodes. The instrument can work at constant current selected in the range of 3-20 mA (constant currents of 20 mA were used troughout). A E649 model Meterohm stirrer was used and measurements of pH were made using a Meterohm 625 pH-meter. A FORTUNA autosampler (± 0.05 mL) was used for taking small precise volumes of different sample solutions.

Sodium sulfite, aniline, formaldehyde, potassium bromide and other chemicals were purchased from Merck. All other chemicals were of analytical reagent grade. All solutions were prepared with doubly distilled deionized water.

Stock solutions of aniline, 1×10^{-3} M; KBr, 0.25 M and NaCl 0.1 M were prepared by dissolving appropriate amount of each compound in water. 1000 μg mL^{-1} solutions of different salts were also prepared.

Procedure: 5 mL of sample solutin containing the appropriate amount of the analytes (aniline) solution, 25 mL of 0.25 M of potassium bromide, 8 mL of buffer and 1 mL methyl red indicator solutions and 10 mL ethanol were added to a 100 mL beaker and then titrated with electrically generated Br_2 titrant under selected constant current (20 mA) passed between two flat Pt electrodes. The end-point of the titration was distinguished by colour change of methyl red indicator from red to colourless.

The concentrations of analytes in the sample solution were obtained by the following equation[15],

$$n = it/zF \qquad (1)$$

where 'n' is the number of moles of any component in the sample solution. 't' is the total transition time (the coulometric titration time for one pre-selected constant current chronopotentiometric run), 'z' is the number of electrons for the component under study and 'F' is the Faraday constant.

RESULTS AND DISCUSSION

A few articles about coulometric determination of organic chemical species in mixed solvents are reported in literature[14-18].

In preliminary experiments, it is find that both formaldehyde and acetaldehyde can be used as good masking agents for sulfite[19] and the second component of the solution mixture can be titrated with good accuracy and efficiency. It must be mentioned that both formaldehyde and acetaldehyde have no effect on the coulometric titration time. The results are shown in Table-1. The total titration time needed for analysis depends on the concentration of components in the sample solution. The aniline was determined in the concentration range of 1×10^{-4}–1×10^{-7} moles in the final solution.

TABLE-1
EFFECT OF FORMALDEHYDE AS MASKING AGENTS FOR SULFITE IN THE COULOMETRIC TITRATION OF ANILINE SOLUTIONS (20 mA current)

Sample type	Titration time		RE (%)	RSD (%)
	Theoretical	Experimental		
Blank[a]	0.0	5.0	–	
Blank + formaldehyde[b]	0.0	4.1	–	1.3
Blank + acetaldehyde	0.0	4.2	–	1.7
Sulfite (4.4×10^{-6} mol) + formaldehyde	–	4.2	–	2.0
Aniline (4.45×10^{-6} mol) + formaldehyde	144.73	144.50	-0.15	1.6
Sulfite (4.4×10^{-6} mol) + Aniline (5×10^{-6} mol) + formaldehyde	144.73	145.00	+0.18	1.5

[a]Blank solution: 25 mL of 0.25 M of KBr solution; 1 mL of methyl red solution and 8 mL of buffer solution (pH = 4). [b]1 mL of 1 M formaldehyde is used as masking agent.

For low concentrated solutions, small constant current values as low as 1 mA may be used. By using small constant current, trace analysis can be performed with small relative errors (< 0.1 %). In most analysis we used 20 mA current throughout.

Effect of different buffer solutions (acetate, phosphate and ammonia) in the pH range of 3-10 on the coulometric titration time for component was investigated. The results are given in Table-2 and it is obvious that the buffer of pH = 4 is the optimum pH value for the system under study.

TABLE-2
EFFECT OF DIFFERENT BUFFER SOLUTIONS (pH EFFECT) ON THE COULOMETRIC TITRATION TIME FOR ANILINE SOLUTION (10 mA current)

Sample	pH of buffer	Theoretical time (s)	Experimental time (s)	Relative error (RE %)
Aniline	3	374.5	380.47	+1.59
	4		368.66	-1.55
	5		395.07	+5.49
	6		115.73	-69.09
	7		110.77	-71.25

The influence of salt effect on the coulometric titration time was investigated by adding different concentrations of NaCl solution to the test solution and then runing the experiment. Results show that the salt concentration has no considerable effect on the coulometric titration time which means that the proposed method can be used for samples with high salt concentration.

In order to study the influence of various cations, anions and molecules on the determination of aniline concentration (1 × 10^{-5}), different amounts of foreign ions or molecules were added to the test solution and the recommended procedure was followed. The results show that Cl^-, NO_3^-, Na^+, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, Li^+, Cu^{2+}, Zn^{2+}, Ce^{4+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, NH_4^+, Al^{3+}, Br^-, OH^-, CH_3COO^-, ClO_3^-, Ag^+, Fe^{2+}, $Cr_2O_7^{2-}$, Mo^{2+}, CO_3^{2-} and ClO_4^- have no considerable effect on the determination of aniline. $S_2O_3^{2-}$, SO_3^{2-}, N_2H_4, NO_2^-, C_6H_6O and $C_8H_{11}N$ have considerable effect on the determination of aniline.

ACKNOWLEDGEMENT

The authors express their appreciation to the Science and Research Center Council of Islamic Azad University in Ahvaz, for financial support of this work.

REFERENCES

1. D.T. Sawyer, A. Sobkowiak and J.L. Roberts, Electrochemistry for Chemists, John Wiley & Sons: New York, edn. 2, Ch. 4 (1995).
2. K. Abresch and I. Claassen, Coulometric Analysis, Chapman and Hall, London, EC4 (1965).
3. J.E. Harrar, Techniques, Electroanalytical Chemistry, Marcel Dekker, New York (1975).
4. S. Oliveri-Vigh, J.J. Donahue, J.E. Heveren and B.Z. Senkowski, *J. Pharm. Sci.*, **60**, 1851 (1971).
5. S.A. Moros, C.M. Hamilton, S. Oliveri-Vigh, J.J. Donahue and J.E. Heveren, *J. Pharm. Sci.*, **64**, 1229 (1975).
6. H. Rajantie and D.E. Williams, *Analyst*, **126**, 86 (2001).
7. W. Ciesielski, U. Zlobinska and A. Krenc, *Chem. Analityczna*, **46**, 397 (2001).
8. P.T. Kissinger and W.R. Heineman, Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, Ch. 4 and 20 (1984).
9. D.R. Shankaran and S.S. Narayanan, *J. Fresenius Anal. Chem.*, **365**, 663 (1999).
10. R. Nakata, S. Okazaki and T. Fujinaga, *Nippon Kagaku Kaishi*, 1615 (1980).
11. D.J. Curran and T.P. Tougas, *Anal. Chem.*, **56**, 673 (1984).
12. E. Beinrohr, M. Cakrt, J. Dzurov, P. Kottas and E. Kozakova, *J. Fresenius Anal. Chem.*, **356**, 253 (1996).
13. O.T. Guenat, W.E. Morf, B.H. van der Schoot and N.F. de Rooij, *Anal. Chim. Acta*, **361**, 261 (1998).
14. E. Beinrohr, M. Cakrt, J. Dzurov, L. Jurica and J.A.C. Broekaert, *Electroanalysis*, **11**, 1137 (1999).
15. V.N. Zyqan, I.P. Viter and A.I. Kamenev, *J. Anal. Chem.*, **49**, 1170 (1994).
16. J.M. Zen and Y.S. Ting, *Anal. Chim. Acta*, **342**, 175 (1997).
17. Z.B. Zhou and C.C. Liu, *Sens. Actuators B*, **52**, 219 (1998).
18. J. Hu, X.Z. Si and H.H. Ma, *Chin. J. Anal. Lab.*, **19**, 90 (2000).
19. R.T. Morrison and R.N. Boyd, Organic Chemistry, Allyn and Bacon, edn. 4, p. 736 (1983).

(*Received*: 27 September 2008; *Accepted*: 25 February 2009) AJC-7280