Journal of the Korean Chemical Society
2010, *Vol. 54, No. 5*
Printed in the Republic of Korea
DOI 10.5012/jkcs.2010.54.5.497

속보

반사 분광기법을 차용한 시차 은법적정을 통한 할로겐 음이온의 정량

황훈[†] · 엄인용*
[†]강원대학교 자연과학대학 화학과
대구가톨릭대학교 생명화학과
[†]Department of Chemistry, Kangwon National University, ChunChon 192-1, Korea
Department of Life Chemistry, Catholic University of Daegu, Gyeongsan 712-702, Korea
(접수 2010. 1. 25; 수정 2010. 7. 27; 게재확정 2010. 8. 5)

Differential Argentometric Titration Equipped with a Reflectance Detector for the Determination of Halogen Anions

Hoon Hwang[†] and In-Yong Eom*
[†]Department of Chemistry, Kangwon National University, ChunChon 192-1, Korea
*Department of Life Chemistry, Catholic University of Daegu, Gyeongsan 712-702, Korea. *E-mail: einyong@cu.ac.kr*
(Received May 25, 2010; Revised April 6, 2010; Accepted August 20, 2010)

주제어: 은법적정, 시차적정, 반사분광법, 할로겐 음이온 정량

Keywords: Argentometric Titration, Differential titration, Reflectance detector, Determination of Halide Anions

INTRODUCTION

An aqueous solution containing Cl^-, Br^- or I^- ion produces a precipitate of characteristic color upon addition of the solution containing Ag^+ ion: AgCl (white), AgBr (creamy), and AgI (yellow), respectively. Such characteristic colors can be used for qualitative identification of a corresponding halide ion, but it is not easy to quantify each constituent ion in various mixtures of halide ions. While several methods for the determination of halide ions in aqueous samples using electrochemical,[1-3] optical,[4] and chromatographic[5-7] techniques have been reported, they all require sophisticated devices and involve complex procedures. The method presented in this paper introduces a relatively simple technique utilizing a stopped flow argentometric titration system equipped with a reflection detector[8-12] for the analysis of aqueous binary mixtures of Br^- and I^- ions.

System for Argentometric Titration Equipped with a Reflectance Detector.

Figure 1 shows a schematic diagram of the system used in this work. A quartz vessel (E) containing 40.0 mL of the titrand (an aqueous mixture of Br^- and I^- ions) (I) is placed in a dark compartment (D) built to block incoming external light. As the titrant (0.101 M $AgNO_3$) is introduced from a 50-mL burette (A) into the titrand through a solenoid valve (B, two-way, 24 V DC) which is controlled by the programmable timer (C), the precipitation reaction begins to produce characteristic silver halide precipitates. The timer has been

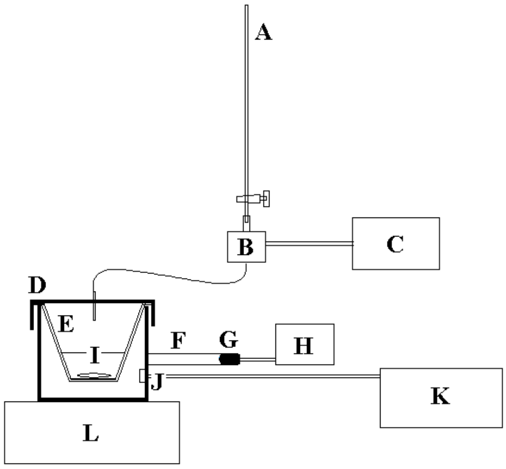

***Fig.* 1.** Schematic diagram of the argentometric titration system equipped with a reflectance detector. A: burette for $AgNO_3$ solution, B: 2-way solenoid valve, C: DC voltage source for the solenoid valve, D: black compartment with a lid, E: quartz container for the titrand, F: glass tubing the light guard, G: blue light emitting diode as the radiation source, H: DC voltage source for the LED, I: the titrand with a teflon coated magnet, J: Si-photodiode as the radiation detector, K; recorder, L: magnetic stirrer.

programmed to switch the solenoid valve ‘ON’ only during the first two seconds (flow rate of 3.36 mL/min) in every one minute for the discrete additions of Ag^+ ion into the titrand. The light from the radiation source (G, high luminescence blue light emitting diode) was guided through a glass tubing (F, i.d.: 4.5 mm) which is shed on the outer surface of the vessel throughout the titration. Then, the intensity of the reflected light is measured at the radiation detector (J, a blue sensitive photodiode) placed on the same side with the radiation source and is recorded (K, sensitivity: 20 mV, chart speed 30 cm/hr).

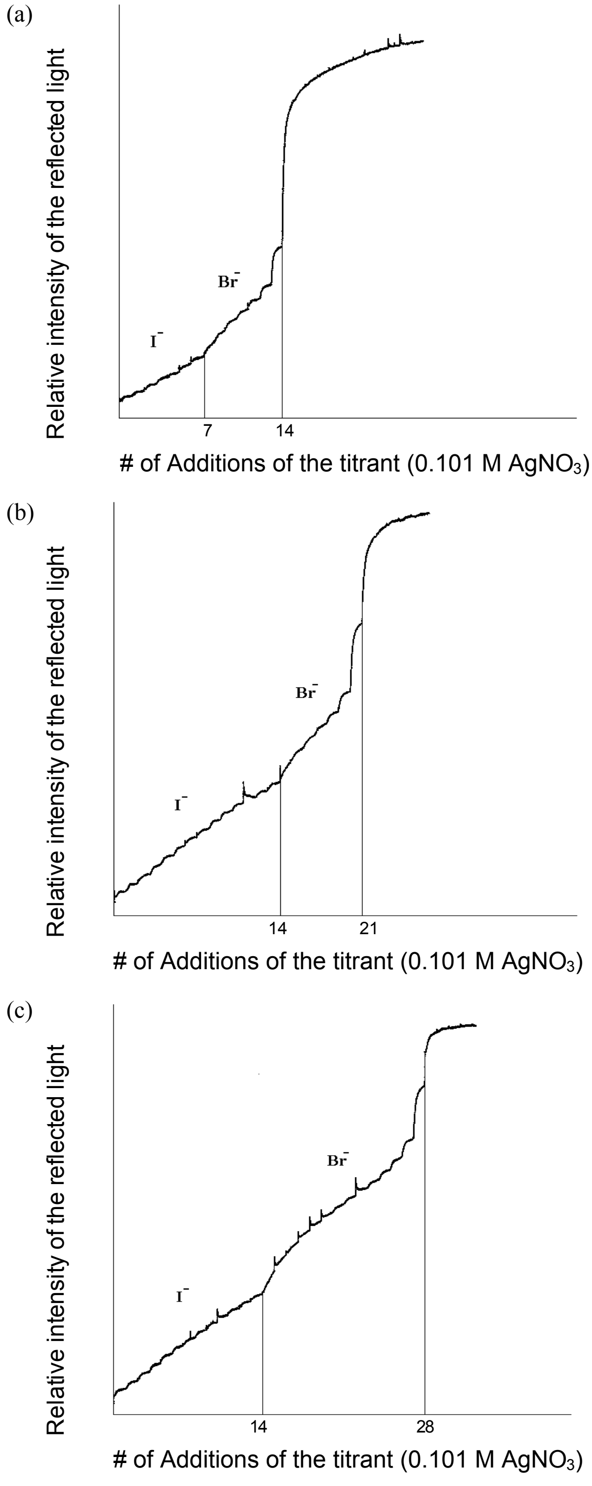

Fig. 2. Titration Curves Obtained With Various Binary Mixtures of Bromide and Iodide Ions. (a) $[I^-] = [Br^-] = 2.00$ mM, (b): $[I^-] = 4.00$ mM, $[Br^-] = 2.00$ mM, (c) $[I^-] = 4.00$ mM, $[Br^-] = 4.00$ mM

Titration Curves.

Figure 2 shows titration curves (relative intensity of the reflected light *vs.* # of additions of the titrant) obtained with various mixtures of bromide and iodide ions. By carefully observing those titration curves, one could find a couple of characteristic patterns which could be used to quantitatively identify each constituent ion in various I^-/Br^- mixtures. First, as the titration begins, the first precipitating I^- ion begins to react with Ag^+ ion to form AgI particles which turn the initially transparent colorless solution into a yellowish colloidal solution and the resulting reflected light shows a gradual stepwise increase due to discrete additions of the titrant of Ag^+. Second, as the first precipitation reaction of I^- ion with Ag^+ ion comes near to a completion; the second precipitation reaction of Br^- ion with Ag^+ ion starts to produce relatively larger stepwise increases in the intensity of the reflected light because of the formation of creamy AgBr particles. Three different Br^-/I^- aqueous mixtures were tested to show that the proposed technique could be feasible for quantitative analysis of halide ions in the aqueous samples. *Figure* 2-(a) is a titration curve obtained with the aqueous mixture of $[Br^-] = [I^-] = 2.00$ mM and consists of two distinct parts. The first part of the curve is attributed to the formation of AgI colloidal solution and shows 7 stepwise linear increases in the intensity of the reflected light. Since the amount of Ag^+ ion added into the analyte soltuion during each step has been found to be 0.0113 mmole, the concentration of I^- ion in the mixture found by counting the number of steps formed in the first linear part of the curve and subsequent calculations was 1.94 mM. The second part of the curve in Figure-(a) shows a pattern of relatively larger stepwise increases in the intensity of the reflected light and was due to the formation of creamy AgBr colloidal solution which has higher reflectivity to the blue LED light source compared to the yellow AgI yellowish particles. The number of steps of the second part of the curve was counted that the last step should be the one formed with the first large relative increase in its height. The bigger jump of the last step may be due to the exponential relationship between the reflected light and the concentration of an analyte.[8] The number of steps formed in the second part of the curve was counted to be 7 and the concentration of Br^- ion in the mixture was found to be 1.94 mM. *Figure* 2-(b) shows the titration curve obtained with a mixture of $[Br^-]$ = 2.00 mM and $[I^-]$ = 4.00 mM and reveals the similar pattern as the curve shown in *Figure* 2-(a). The number of steps formed during the first linear part of the curve was counted to be 14 and was due to the doubled concentration of I^- ion while the second part of the curve remained as the same as the one in *Figure* 2-(a). *Figure* 2-(c) shows the titration curve obtained with a mixture of $[Br^-]$ = 4.00 mM and $[I^-]$ = 4.00 mM so the number of steps for both parts are doubled.

In summary, a simple technique of differential argentometric titration utilizing the relative intensity of reflected light has been proved to be feasible for the quantitative analysis of Br^- and I^- ions in their aqueous mixtures. Since the current work has been limited to millimolar concentration (mM) range of the two ions, further works on the wider concentration ranges are required.

REFERENCES

1. Arkhangel'skaia, A. S.; Khomik, L. I. *Klin Lab Diagn* **1994**, *4*, 11
2. Ni, Y.; Wu, A. *Anal. chim. acta* **1999**, *390*(3), 117
3. Prest, J. E.; Fielden, P. R. *J. of Analytical and Bioanalytical Chem*. **2005**, *382*(5), 1339
4. Chris D. et. al. *J. of Fluorescence* **1999**, *9*(3), 163
5. Przeszlakowski, S. and Kocjan, R., *Chromatographia*, **1980**, *13*(3), 175
6. Wang , L.-H. *J. of Chromatographic Sci*. **2002**, *40*(6), 326
7. Hwang, H. *Bull. Korean Chem. Soc*. **2007**, *28*(5), 721.
8. Hwang, H.; Jung, D. *J. of Korean Chem. Soc*. **2000**, *44*(4), 316
9. Hwang, H.; Jung, S.; Lee, K. *J. of Korean Chem. Soc*. **2001**, *45*(1), 45
10. Hwang, H. *J. of Korean Chem. Soc*. **2001**, *45*(6), 513.
11. Hwang, H. *J. of Korean Chem. Soc*. **2002**, *46*(5), 471.
12. Lee, J.-H.; Han, M.-A.; Kang, S.-W.; Seo, S.-S.; Hwang, H. *Bull. Korean Chem. Soc*. **2005**, *26*(1), 36.