Microchemical Journal 114 (2014) 203–209

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Certified reference material for ammonium ions in high-purity ammonium chloride: Influence of pH on coulometric titration of ammonium ions with electrogenerated hypobromite

Toshiaki Asakai *, Toshihiro Suzuki, Tsutomu Miura, Akiharu Hioki

National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan

ARTICLE INFO

Article history:
Received 13 December 2013
Accepted 1 January 2014
Available online 10 January 2014

Keywords:
Coulometric titration
Oxidation–reduction titration
Precipitation titration
Electrogenerated hypobromite
Certified reference material
Ammonium chloride

ABSTRACT

No report has been published concerning reference materials of ammonium chloride in which ammonium ions were accurately determined, though ammonium chloride is widely used as a standard of ammonium ions. In the present paper, accuracy of the coulometric titration of ammonium ions with electrogenerated hypobromite was studied. The authors found that the pH of electrolyte solution significantly affected the accuracy of the assay of ammonium ions. Lower assays were obtained at pH more than 8.5 or less than 8.0: much higher pH values led to evaporation of ammonia and much lower pH ones led to insufficient hypobromite generation or insufficient conditional equilibrium constant of the reaction between ammonium ions and hypobromite. Ammonium ions in ammonium chloride were certified by coulometric titration under an appropriate condition, and chloride ions in it were also certified by gravimetric titration based on standard sodium chloride. The first certified reference material with ammonium assay was developed which enabled more accurate ammonium determination than that before.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Ammonium chloride is widely used as a standard of ammonium ions in analyzing different materials such as fertilizers, drugs, additives and analytical reagents. The purity of ammonium chloride has been usually evaluated by determining its chloride content since the accurate assay of ammonium ions is not easy. One of the authors reported the precise coulometric titration of ammonia and ammonium ions with electrogenerated hypobromite [1]. In the previous report, ammonia and ammonium ions were assayed by coulometric titration based on both acidimetry and oxidimetry, and highly accurate assays were presented. However, the apparent assays were corrected by extrapolating the time required for electrolysis to zero because those proportionally decreased with the time. This phenomenon would be caused by the diffusion of ammonium ions from the generator-electrode chamber to the counter one of the coulometric titration cell or by something else. The coulometric titration cell in the previous report did not have intermediate compartments between the generator-electrode chamber and the counter-electrode one; therefore, any diffusion loss of the sample was not avoided. This phenomenon was one of the major problems to be solved.

Ammonia or ammonium ions react with hypobromite in an alkaline solution based on the following reaction [2]:

$$2NH_4^+ + 3BrO^- + 2OH^- \rightarrow N_2 + 3Br^- + 5H_2O. \quad (1)$$

Coulometric titration directly determines the amounts of substance by measuring the electric charge (electrical current and time) in an electrochemical reaction based on Faraday's law. The coulometric titration with the electrogenerated hypobromite could be utilized to determine nitrogen compounds including ammonia and ammonium salts [1,3–6].

In the present study, the authors found that the pH of electrolyte significantly affected the accuracy of the assay of ammonium ions by the coulometric titration with electrogenerated hypobromite. Finally, the assay of ammonium ions in ammonium chloride was determined with the coulometric titration under an appropriate condition, and the assay of chloride ions in it was also determined with gravimetric titration with standard sodium chloride. The drying condition for ammonium chloride was also examined.

2. Materials and methods

General techniques were similar to those in the previous report [1]. Ammonium chloride was of analytical reagent grade (25 g each, 200 bottles) obtained from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Analytical reagent grade chemicals were used unless otherwise stated in the present paper. The Faraday constant was 96,485.3365 C mol^{-1} [7]. The molar mass of ammonium chloride was 53.4903 g mol^{-1} [8].

---

* Corresponding author. Tel.: +81 29 861 6881; fax: +81 29 861 6890.
E-mail address: t-asakai@aist.go.jp (T. Asakai).

0026-265X/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.microc.2014.01.001

Air buoyancy corrections were always applied; the density used for the purpose was 1.519 g cm^{-3} for ammonium chloride [9].

The instruments for coulometric titration consisted of a constant current source, a custom-built switch, standard resistors, a voltmeter and a universal counter [10,11]. The end-point was detected by constant-voltage biamperometry, which consisted of a DC source and a digital multimeter with a dual platinum-plate electrode (each 5 mm × 5 mm). Constant voltage (150 mV) was applied between the platinum pair of the electrode, and the current was monitored.

The coulometric titration cell was a horizontal type with two intermediate compartments separated by three sintered glass filters placed between the generator-electrode chamber and the counter-electrode one to avoid any loss of analyte as a result of diffusion from the generator-electrode one (Fig. 1). The electrodes were a platinum cylindrical plate (circumference: 80 mm, height: 25 mm, supporting rod: 1 mm ϕ × 150 mm long) as a generator electrode and a platinum wire (1.5 mm ϕ × 300 mm long) as a counter one.

The salt bridge for the coulometric titration cell was a 3% (mass fraction) agar gel containing 3% (mass fraction) sodium sulfate. The anolyte consisted of 1 mol L^{-1} sodium bromide and 10 g L^{-1} sodium tetraborate decahydrate, and the catholyte had the same composition as that of the anolyte except sodium bromide. The pH of anolyte was adjusted with sulfuric acid and sodium hydroxide.

A plastic syringe with a perfluoroalkoxy (PFA) or polyetheretherketone (PEEK) needle was used for gravimetric titration of ammonium chloride with a silver nitrate solution standardized based on sodium chloride and gravimetric introduction of a solution-form sample to the coulometric titration cell.

3. Results and discussion

3.1. Influence of experimental time and pH on ammonium ion assay by coulometric titration

One of the authors reported the purity of ammonium chloride by extrapolating the time required for electrolysis to zero in the previous report [1], because the apparent assays proportionally decreased with the experimental time. To evaluate the dependence of the apparent assay on the experimental time in the present study, ammonium ions were determined under different conditions on pH of electrolyte and delay time (Fig. 2). An approximately 35 mmol kg^{-1} (mmol kg^{-1} means amount of substance per mass of solution not solvent throughout the present paper) sample solution was prepared by dissolving ammonium chloride in water. Approximately 3 g (*ca.* 0.1 mmol) of the sample solution was analyzed by coulometric titration using a long large constant current (60 mA) to electrolyze most of the sample and subsequently short small constant currents (10 mA, 2 s) to draw the titration curve around the end point.

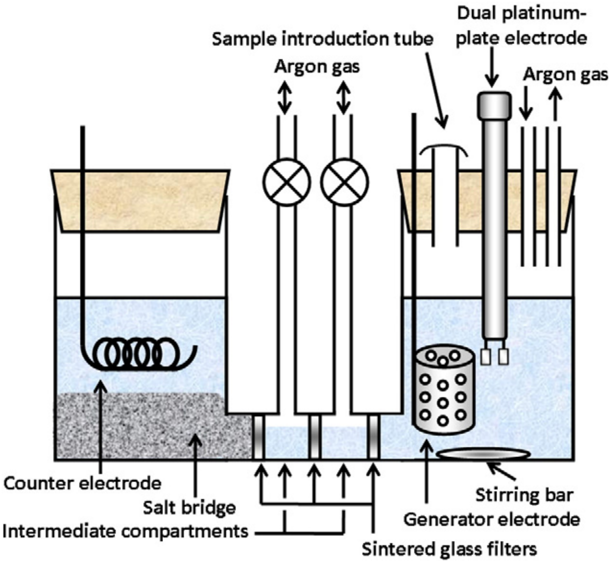

Fig. 1. Horizontal type coulometric titration cell with two intermediate compartments separated by three sintered glass filters.

The examination shown in Fig. 2(a) was done to find the cause of the disappearance of ammonium with the experimental time. Delay time was the duration before electrolysis after the sample addition. The pH value of all electrolytes in Fig. 2(a) was 8.5 before electrolysis. The decrease rates of apparent ammonium assay became larger under the condition of stronger argon (purity of *ca.* 99.995%) purging. Though the decrease rate was slightly smaller when there were no electrolyte solutions in the intermediate compartments during the delay time, there was still a large decrease. Judging from the examination, most of ammonium ions did not diffuse from the generator-electrode chamber to the counter-electrode one but evaporated together with argon gas flow. The apparent assays at no delay time were roughly in agreement for those under all conditions; "no delay time" means that electrolysis is started within 30 s after sample addition. Ammonium ions had partly disappeared during the electrolysis; however, the disappearance had only limited effects within the repeatability on the assay because the electrolysis time at 60 mA was about 7 min for 0.1 mmol of ammonium ions and also the amount of substance of the disappearance for 7-min electrolysis substantially corresponded to that for less than half of 7-min delay time.

To confirm the presence of ammonia in the outlet flow of argon gas after passing through the coulometric titration cell, pH of trap water for the argon gas was monitored. The pH was stable for the argon gas after passing through the coulometric titration cell with only electrolyte, and increased for the argon gas from the coulometric titration cell with electrolyte and ammonium chloride. Therefore, the presence of ammonia in the argon-gas flow during the delay time was confirmed. The pH values of electrolyte were naturally expected to be a key factor in the evaporation of ammonia. The examination shown in Fig. 2(b) was done to evaluate the influence of the pH of electrolyte on apparent ammonium assay; argon-gas flow was not used in this examination. The investigation yielded results as expected: the decrease rates of apparent ammonium assay were smaller using electrolytes with lower pH. Under the appropriate condition (electrolysis current 60 mA, no delay time, pH 8.0 to 8.5 and no argon-gas purging), the disappearance rate of ammonium ions given in Fig. 2(c) was approximately 0.001% a minute; the influence of the delay time of 10 min was within the repeatability and no extrapolating was necessary.

The results depicted in Fig. 3 are apparent assays of ammonium ions (*ca.* 0.1 mmol) expressed as ammonium chloride at the different pH values of electrolyte without delay time. Each apparent assay was plotted against both pH values before the sample addition and after analyzing the sample. The assays had a maximum around pH 8.0 to pH 8.5. The lower assays were understood as a result of the evaporation of ammonia at higher pH values and the insufficient hypobromite electrogeneration or insufficient conditional equilibrium constant at lower pH values. The apparent assay at initial pH 7.4 before the sample addition was less than 98%. Electrogeneration of bromine might be significant at pH lower than 7.5 before the sample addition though there was no clear evidence of bromine generation; as a matter of fact, the inaccurate assays were obtained.

Dependency of apparent assays of ammonium ions expressed as ammonium chloride on amounts of substance of ammonium chloride is shown in Fig. 4. The results were obtained under the following condition: electrolysis current 60 mA, no delay time, initial pH 8.5 and no argon-gas purging. There was no significant dependency on the sample size.

Download English Version:

https://daneshyari.com/en/article/7643332

Download Persian Version:

https://daneshyari.com/article/7643332

Daneshyari.com