Reliability in standardization of sodium thiosulfate with potassium dichromate

Toshiaki Asakai *, Akiharu Hioki

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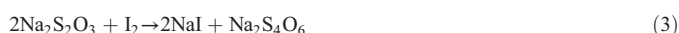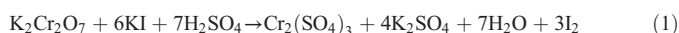
ARTICLE INFO

ABSTRACT

Sodium thiosulfate is often standardized with potassium dichromate. In the standardization, iodine (triiodide) liberated by potassium dichromate in an acidic potassium iodide solution is titrated with a sodium thiosulfate solution. The iodine liberation process significantly affects the titration results. In the present study, the accuracy of the liberation process was examined by assaying potassium dichromate through two different paths: assaying directly by coulometric titration with electrogenerated Fe(II), and assaying by gravimetric titration through the iodine liberation reaction with a sodium thiosulfate solution of which concentration was standardized by coulometric titration with electrogenerated iodine. The accuracy of the standardization of a sodium thiosulfate solution by potassium dichromate was discussed from the apparent assays of potassium dichromate under different measurement conditions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Sodium thiosulfate is a useful reducing agent for a titrant solution in volumetric analyses such as iodometry and the Winkler method to measure dissolved oxygen [1,2]. Oceanography community requires the accuracy and the reproducibility of the measurements of dissolved oxygen; the accurate standardization procedure of sodium thiosulfate is needed. The agent is often standardized with potassium dichromate and, on the other hand, is usually standardized with potassium iodate in Japan [3–6]. Iodine (triiodide ions) liberated by potassium dichromate or potassium iodate in an acidic potassium iodide solution is titrated with a sodium thiosulfate solution to standardize the thiosulfate [reactions (1), (2) and (3)].

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2 \quad (1)$$

$$KIO_3 + 5KI + 3H_2SO_4 \rightarrow 3K_2SO_4 + 3H_2O + 3I_2 \quad (2)$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \quad (3)$$

The iodine liberation process is significantly affected by the amounts of acid and potassium iodide added, the waiting time for the liberation, and light; therefore, the process plays a key role for the accuracy of standardization of sodium thiosulfate. The authors reported an accurate standardization procedure for a sodium thiosulfate solution with potassium iodate [7].

It has been pointed out that there are some biases in the standardization of sodium thiosulfate with potassium dichromate [3,8–12]. Some researchers reported that excess consumption of thiosulfate occurred in an acidic medium due to air oxidation of iodide ions [8,9]. Hahn described that the main reason of the excess consumption of thiosulfate in a weak acidic medium was not air oxidation of iodide, but a complex between Cr(III) and thiosulfate, which reacted with iodine slowly [3,12]. Kolthoff and Belcher reviewed the studies on the titration procedure [3] and mentioned the appropriate conditions to ensure complete and stoichiometric reaction with dichromate: the hydrogen ions concentration 0.2 mol L^{-1} to 0.4 mol L^{-1}, 2% of potassium iodide, and standing for 10 min to 15 min before starting titration with thiosulfate.

The impact of the biases has remained obscure because the accuracy of the standardization of thiosulfate has been discussed by using relative methods for conventional titration. Thiosulfate is usually standardized with sublimed iodine whose purity is hypothetically regarded as 100%. In the present study, the accuracy of the standardization was absolutely evaluated by coulometric titration (Fig. 1). Coulometric titration absolutely yields an accurate oxidimetric–reductometric assay based on Faraday's Law. The accuracy of the iodine liberation process was examined by comparing two assays of potassium dichromate using different

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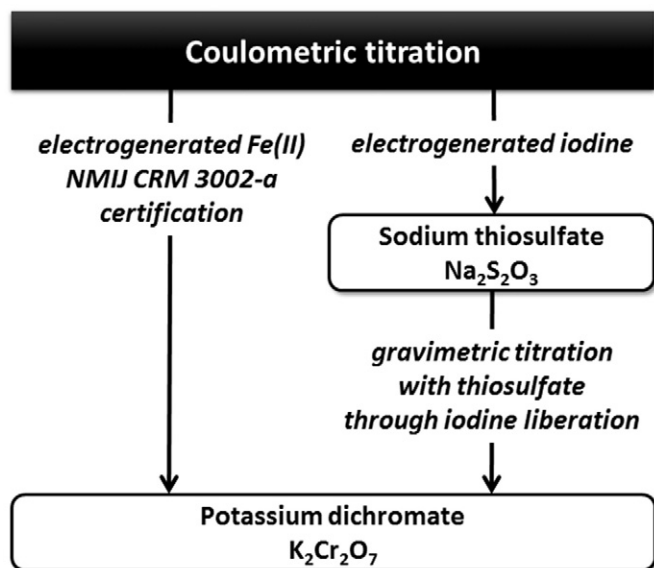E-mail address: t-asakai@aist.go.jp (T. Asakai).

Fig. 1. Experimental design for the assay of potassium dichromate to investigate the iodine liberation reaction.

titrations based on coulometric titration. Firstly, potassium dichromate was directly assayed by coulometric titration with electrogenerated Fe(II) [13]. Secondly, potassium dichromate was assayed by gravimetric titration through the iodine liberation reaction with a sodium thiosulfate solution, of which concentration had been standardized by coulometric titration with electrogenerated iodine. The accuracy of the standardization of a sodium thiosulfate solution by potassium dichromate was discussed from the apparent assays of potassium dichromate under different measurement conditions.

2. Material and methods

Constant-voltage biamperometry (a dead stop method) was utilized to measure the amount of liberated iodine under several conditions as a preliminary experiment. A DC source and a digital multimeter with a dual platinum-chip electrode (each platinum chip: 0.5 mm $\phi \times$ 0.5 mm long) were used for constant-voltage biamperometry. Constant voltage was applied between the platinum pair, and the current was monitored. The current had good proportionality to the amount of liberated iodine [7]. A dual platinum-plate electrode (each 5 mm × 5 mm) was used in gravimetric titration to increase sensitivity as described previously [7, 13–15].

The experimental set-ups and the procedures of coulometric titrations for potassium dichromate and a sodium thiosulfate solution were described previously [7,13–15]. As described in the previous report [13], high purity potassium dichromate as a certified reference material (CRM) was established by coulometric titration with electrogenerated Fe(II). The certified value (mass fraction) of the CRM, NMIJ CRM 3002-a, is 99.974% ± 0.011%, where the value following ± indicates the expanded uncertainty with the coverage factor 2.

Gravimetric titration was carried out to assay potassium dichromate with a sodium thiosulfate solution through the iodine liberation reaction in the following procedure: approximately 0.2 g of potassium dichromate were placed in a 200 mL tall beaker, it was dissolved in 100 mL of water, potassium iodide and 9 mol L^{-1} sulfuric acid were added, and the solution was titrated with a sodium thiosulfate solution. The concentration of the sodium thiosulfate solution was standardized in advance by coulometric titration with electrogenerated iodine [7]. A plastic syringe with a PEEK needle was used to weigh the sodium thiosulfate solution. Potassium dichromate was weighed with resolution of

1 μg, and potassium iodide and solutions were weighed with resolution of 10 μg.

3. Results and discussion

3.1. Determination of sodium thiosulfate by coulometric titration and uncertainty estimation

The concentration of a sodium thiosulfate solution (3 g to 8 g) standardized by coulometric titration was, for example, 208.653 mmol kg^{-1} (RSD 0.007%, $n = 5$) ('RSD' means 'relative standard deviation', and 'n' is the number of measurements under a repeating condition). The uncertainty sources for the concentration of the solution (ca. 3 g of ca. 200 mmol kg^{-1}) were as follows (the number in each parenthesis indicates the relative standard uncertainty): repeatability (0.0032%, RSD of the mean, $n = 5$), Faraday constant (0.000 002 2%), a standard resistor (0.000 65%, calibration and the influence of temperature), a frequency counter (0.000 05%), a voltmeter (0.000 15%) and weighing (0.0019%, sensitivity and linearity of the balance). Finally, the combined standard uncertainty was 0.0038% relative and the expanded uncertainty with a coverage factor 2 was 0.0076% relative. The coulometric titration allowed the authors to discuss the accuracy of the iodine liberation reaction by potassium dichromate in the order of magnitude of 0.01%. A sodium thiosulfate solution is stable enough to be required in the present study [16,17].

3.2. Influence of the amount of potassium iodide added

Approximately 0.2 g of potassium dichromate were dissolved in 100 mL of non-deaerated water followed by adding 1 g to 6 g of potassium iodide and 1 mL of 9 mol L^{-1} sulfuric acid in turn; after the acid addition, iodine liberation started. The iodine liberation process monitored by constant-voltage biamperometry using a dual platinum-chip electrode (applied constant-voltage 500 mV) is shown in Fig. 2; the indicator current corresponds to the amount of iodine liberation. Under the condition using 1 g to 2 g of potassium iodide and 1 mL of 9 mol L^{-1} sulfuric acid, lacking of iodide ions in the solution led to the deposition of solid iodine, and the indicator current drastically decreased in unforeseeable timing after the initial increase. Under the conditions using 3 g to 6 g of potassium iodide and the same amount of sulfuric acid, the
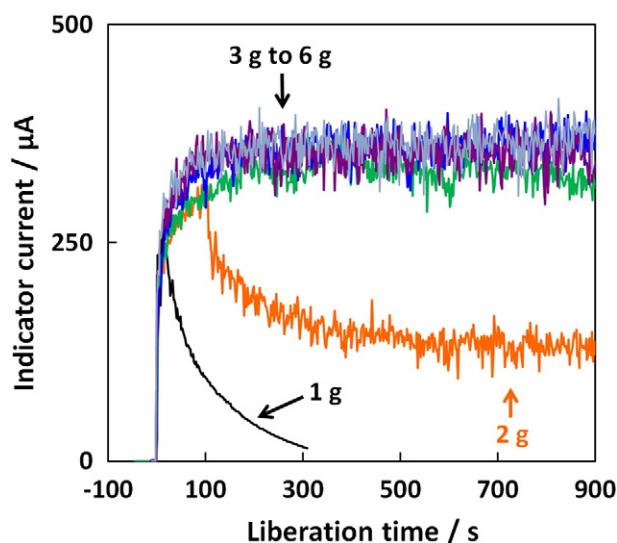

Fig. 2. The iodine liberation process monitored by constant-voltage biamperometry for 0.2 g of potassium dichromate using a dual platinum-chip electrode (applied constant-voltage 500 mV), stirring at 900 revolutions per minute (rpm). The sample was dissolved in 100 mL of non-deaerated water, and 1 g to 6 g of potassium iodide and 1 mL of 9 mol L^{-1} sulfuric acid were added.