Characterization of oxyanions of chlorine by multipath titrimetric approach for drinking water quality control

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Abstract. The analysis of oxyanions, perchlorate, chlorate, chlorite and hypochlorite ions, is of interest, especially from the viewpoint of evaluating drinking water quality. Instrumental analyses are generally performed to quantify them, and require a standard solution of corresponding ions; however, no standard solutions characterized by a metrologically valid procedure have existed. In the present study, perchlorate, chlorate and chlorite ions were characterized by performing multipath titration techniques. This technique is an approach to determine the amount of substances in chemicals by employing different stoichiometric reactions. It has decreased the risk and the contribution of unknown biases that each measurement method has, and gives further reliable results than those based on a conventional single titration method. The comprehensive evaluation of the measurement uncertainties for these assays was carried out, resulting in the establishment of the measurement methodologies for oxyanion standards.

1. Introduction
Perchlorate, chlorate, chlorite and hypochlorite ions are placed in the category of oxyanions of chlorine. The risk and the behavior of these ions in the environment, and the residues in foods and drinking water are of interest in recent years. Against these situations, several institutions such as the World Health Organization have issued documents to examine oxyanion contents in water [1]. The measurements of oxyanions are also required by the Japanese Water Supply Act established by a Japanese ministry, the Ministry of Health, Labour and Welfare [2].

Perchlorate, chlorate and chlorite ions have been generally determined by instrumental analyses such as electrochemical methods, colorimetry, ion chromatography and flow injection analysis. These instruments used to quantify them require a standard solution of corresponding ions; however, no standard solutions have existed, which were characterized on a metrologically valid procedure.

The author has evaluated several materials such as osmium and cerium compounds by performing multipath titration techniques. This technique is an approach to determine the amount of substances in chemicals by employing different stoichiometric reactions. It has decreased the risk and the contribution of unknown biases that each measurement method has, and gives further reliable results than those based on a conventional single titration method.

Characterizations of perchlorate and chlorate ions by a multipath titrimetric approach have been reported [3, 4]. The techniques applied to the characterizations are:
- Acidimetric coulometric titration with cation exchange resin, redox gravimetric back titration with titanium(III), and precipitation gravimetric titration with silver(I) for perchlorate ions;
- Gravimetric back titration with dichromate and iron(II), precipitation gravimetric titration with silver(I) after decomposition of chlorate, and redox gravimetric titration with thiosulfate through an iodine liberation reaction for chlorate ions.

The assays of certified reference materials (CRMs) which were used to standardize the titrants were determined by primary method of measurement, coulometric titration. Coulometric determinations based on Faraday’s laws of electrolysis as an anchor method are capable to ensure the traceability to the International System of Units (SI) (i.e., mass, time and ampere). All determination procedures presented, are therefore able to ensure the traceability of the mass fraction of perchlorate and chlorate.
ions to the SI. All titrimetric results were in good agreement within their expanded uncertainties; therefore, the measurement methodologies for perchlorate and chlorate ions as a CRM have been established.

This paper focuses on establishing a measurement methodology for chlorite ions by a multipath titrimetric approach. Chlorite is used as a disinfection agent and often found during disinfection processes for vegetables, drinking water and foods. The dissemination and the development of the reliable CRM has been highly demanded.

2. Principle of titrimetric reactions

The experimental design for chlorite ion determinations performed is depicted in Figure 1.

Path A – redox titration with thiosulfate standardized with standard potassium iodate

Iodine (triiodide) liberated by oxidants such as chlorite ions in an acidic potassium iodide solution can be titrated with a sodium thiosulfate solution [5]. The sodium thiosulfate solution is standardized with standard potassium iodate through a similar iodine liberation reaction.

\[
\begin{align*}
\text{ClO}_2^- + 4\text{I}^- + 4\text{H}^+ & \rightarrow 2\text{I}_2 + \text{Cl}^- + 2\text{H}_2\text{O} \\
2\text{S}_2\text{O}_3^{2-} + \text{I}_2 & \rightarrow 2\text{I}^- + 3\text{S}_2\text{O}_4^{2-}
\end{align*}
\] (A.1) (A.2)

\[
\begin{align*}
\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ & \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \\
\text{Path A} & \quad \text{Path B} & \quad \text{Path C}
\end{align*}
\] (A.3)

Path B – redox back titration with iron(II) standardized with standard potassium dichromate

Excess iron(II) standardized with potassium dichromate is added to oxidants, and then the excess iron(II) is back-titrated with potassium dichromate [6].

\[
\begin{align*}
\text{ClO}_2^- + 4\text{Fe}^{2+} + 4\text{H}^+ & \rightarrow \text{Cl}^- + 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \\
6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ & \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\end{align*}
\] (B.1) (B.2)

Path C – precipitation titration with silver(I) standardized with standard sodium chloride after the decomposition of chlorite ions with excess sodium sulfite

The decomposition reaction of chlorite ions by sodium sulfite, a strong reducing agent, is expected to be proceeded according to the reaction (C.1). Chloride ions generated by the decomposition reaction are titrated with a silver nitrate solution standardized with standard sodium chloride [7].

\[
\begin{align*}
\text{ClO}_2^- + 2\text{SO}_3^{2-} + 4\text{H}^+ & \rightarrow \text{Cl}^- + 2\text{H}_2\text{SO}_4 \\
\text{Cl}^- + \text{Ag}^+ & \rightarrow \text{AgCl}
\end{align*}
\] (C.1) (C.2)

3. Material and methods

Sodium chlorite was obtained from Alfa Aesar, MA, USA. The following constants were used for the material: molar mass 90.440 g mol\(^{-1}\) (IUPAC Atomic weights of the elements 2013), and density 2.5 g cm\(^{-3}\) for buoyancy corrections [8]. Detailed three CRMs and coulometric determinations were previously reported (NMIJ CRM 3006-a potassium iodate, NMIJ CRM 3002-a potassium dichromate...
and NMII CRM 3008-a sodium chloride). The multipath titrimetry was performed in a similar manner as the previous report [3, 4]. The end-point detection methods used were constant-voltage biamperometry for path A, and potentiometry for paths B and C.

4. Results and Discussion

4.1. Path A – redox titration with thiosulfate standardized with standard potassium iodate

4.1.1. Path A – examinations of iodine liberation reaction by constant-voltage biamperometry

Constant-voltage biamperometry was used to roughly investigate the rate of the iodine liberation reaction (formula A.1). Constant-voltage biamperometry is a method of monitoring the current between twin electrodes where a constant voltage is applied. The current flows in the presence of both iodide and triiodide ions through the reaction $[3I^- \rightarrow I_3^- + 2e^-]$ on each surface, and is proportional up to a certain amount of liberated iodine [5].

Approximately 0.08 g of sodium chlorite was dissolved in ca. 50 mL of pure water. The currents were monitored by using a dual Pt-chip electrode (applied constant voltage 500 mV), stirred at 600 rpm, after adding (a) 1 g, 2 g, 3 g, 4 g or 5 g of potassium iodide with 1 mL of 6 mol L$^{-1}$ hydrochloric acid; (b) 3 g of potassium iodide with 0.5 mL, 1 mL, 2 mL or 3 mL of 6 mol L$^{-1}$ hydrochloric acid. The iodine liberation reactions were apparently completed under the conditions given above except for a condition using 1 g of potassium iodide with 1 mL of 6 mol L$^{-1}$ hydrochloric acid. The reason of the insufficient iodine liberation under the inappropriate condition was a lack of iodide ions in the solution. The smaller amount of iodide ions makes it difficult for liberated iodine to be dissolved in the solution even if the amount of potassium iodide added is theoretically enough to liberate iodine. The liberation reactions seemed to be sufficiently rapid in the appropriate conditions (within a few seconds); no waiting time to liberate iodine and complete the reaction was needed. Considering these examinations, the following condition was adopted: use of 1 mL of ca. 6 mol L$^{-1}$ hydrochloric acid, 3 g of potassium iodide, and no iodine liberation time. Similar biamperometric examinations were performed with sulfuric acid instead of hydrochloric acid: 1 g to 5 g of potassium iodide with 0.5 mL to 3 mL of ca. 9 mol L$^{-1}$ sulfuric acid for 0.08 g of sodium chlorite. The profiles of the iodine liberation were similar to those with hydrochloric acid. Both acids are available to liberate iodine.

This rapid iodine liberation reaction with chlorite ions was similar to those with iodate [5], periodate, bromate and cerium(IV) ions. In contrast, the processes with dichromate [9], chlorate [3] and perchlorate ions [4] were substantially different. With dichromate ions, the iodine liberation reactions with similar amounts of potassium iodide and acids were slower, and were completed more than 10 min. Several factors led to inaccurate results during the waiting time to liberate iodine, such as interactions among iodide, thiosulfate, chromium(III) and iron(II) ions, and air-oxidation of iodide ions. With chlorate ions, the reaction was very slow. Chlorate ions required highly acidic conditions to oxidize iodide ions, e.g., use of undiluted 6 mol L$^{-1}$ hydrochloric acid with 5 g of potassium iodide, and more than 10 min liberation time. With perchlorate ions, the reaction hardly proceeds. Oxynions with more oxygen atoms are more inactive in iodimetric reactions.

4.1.2. Path A – examinations of iodine liberation reaction by titration with thiosulfate ions

Sodium chlorite was assayed by gravimetric titration with thiosulfate ions through different iodine liberation conditions.

The relative standard deviation (RSD) of the concentration of a sodium thiosulfate aqueous solution (ca. 200 mmol kg$^{-1}$) standardized with standard potassium iodate (ca. 0.15 g) was 0.00790 % ($n = 4$, $n$ is the number of measurements under a repeating condition); the RSD of the mean was 0.00395 % ($n = 4$).

Figure 2 illustrates a dependency of sodium chlorite assays on the period of iodine liberation. Approximately 0.1 g of sodium chlorite was dissolved in ca. 50 mL of pure water, and added 3 g of...
potassium iodide and 1 mL of 6 mol L\(^{-1}\) hydrochloric acid. There was no significant dependency of sodium chlorite assays on the waiting time from 0 min to 25 min.

Figure 3 illustrates the dependencies of sodium chlorite assays on the amounts of potassium iodide and 6 mol L\(^{-1}\) hydrochloric acid for ca. 0.1 g of sodium chlorite. No dependency on the amounts of potassium iodide was observed. Smaller assays when using less than 0.5 mL of 6 mol L\(^{-1}\) hydrochloric acid with 3 g of potassium iodide were reasonable because of the stoichiometrically small amount of acids.

Finally, the assay of sodium chlorite calculated from the data obtained with 3 g of potassium iodide and 1 mL of 6 mol L\(^{-1}\) hydrochloric acid without waiting time was 79.560 % (mass fraction). The standard deviation (SD) and RSD of the measurements were 0.258 % and 0.324 % \((n = 9)\), respectively.

**Figures 2 and 3.** Dependencies of sodium chlorite assays on the period of iodine liberation, and on the amounts of potassium iodide and hydrochloric acid.

4.2. **Path B − redox back titration with iron(II) standardized with standard potassium dichromate**

An approximately 300 mmol kg\(^{-1}\) iron(II) was prepared by dissolving iron(II) sulfate heptahydrate in ca. 2 mol L\(^{-1}\) sulfuric acid. Approximately 0.15 g of standard potassium dichromate was dissolved in 20 mL of 2 mol L\(^{-1}\) sulfuric acid, and then titrated with the iron(II) solution on heating around 70 °C. The RSD of the concentration of the iron(II) solution obtained was 0.0203 % \((n = 5)\); the RSD of the mean was 0.00910 % \((n = 5)\).

An approximately 20 mmol kg\(^{-1}\) standard potassium dichromate solution was gravimetrically prepared by dissolving standard potassium dichromate in pure water for back titration. Approximately 0.1 g of sodium chlorite was dissolved in ca. 10 mL of pure water, and added the excess iron(II) solution \((ca. 0.5 \text{ } \% \text{ excess})\). The solution was heated around 70 °C, and then the excess iron(II) was titrated with the standard potassium dichromate solution on heating. It was necessary that sodium chlorite was dissolved in some pure water before adding the iron(II) solution \((2 \text{ mol L}^{-1} \text{ sulfuric acid medium})\) because the solution was colored in yellow by adding the solution directly to sodium chlorite. Adding 2 mol L\(^{-1}\) sulfuric acid without iron(II) made the solution yellow. The yellow color, therefore, could be chlorine dioxide and indicated the change of chlorite ions. A dependency of sodium chlorite assays on the period of heating is given in Figure 4. The redox reaction for sodium chlorite apparently took over 10 min with heating to complete. The average calculated from the data obtained with heating over 10 min was 80.449 % (mass fraction). The SD and RSD of the measurements were 0.254 % and 0.315 % \((n = 7)\), respectively.

4.3. **Path C − precipitation titration with silver(I) standardized with standard sodium chloride after the decomposition of chlorite ions with excess sodium sulfite**

This precipitation-titration path was challenging to apply to assay chlorite ions due to the lower purity of sodium chlorite containing much chloride impurity. The final assays were corrected by using halogen contents in solid sodium chlorite before the decomposition.
Figure 4. Dependency of sodium chlorite assays on the period of heating by back titration with iron(II) and dichromate.

Figure 5. Dependency of sodium chlorite assays on the period of heating by titration for chloride ions generated through the decomposition with excess sulfite. The assays were corrected by using measurable halogen contents containing in solid sodium chlorite.

The RSD of the concentration of a silver(I) nitrate aqueous solution (ca. 300 mmol kg\(^{-1}\)) standardized with standard sodium chloride (ca. 0.2 g) was 0.00431 % (\(n = 4\)); the RSD of the mean was 0.00216 % (\(n = 4\)).

An excess amount of reductants, ca. 20 mL of ca. 1.2 mol L\(^{-1}\) sodium sulfite (ca. 150 g per 1 L), was added to approximately 0.3 g of sodium chlorite. Adding ca. 3 mL of ca. 7 mol L\(^{-1}\) nitric acid (nitric acid / water = 1 / 1 in volume) violently accelerated the decomposition reaction with generating gas and self-heating. The solution was heated at 70 °C to complete the decomposition. After diluting with pure water up to 50 mL, generated chloride ions were titrated with the silver(I) solution. Figure 5 illustrates a dependency of sodium chlorite assays on the period of heating. There was no dependency on the reaction time; therefore, sodium chlorite was completely decomposed in all presented conditions. The precipitation assay of sodium chlorite after the decomposition was 106.982 % (mass fraction); the SD and RSD of the measurements were 0.179 % and 0.167 % (\(n = 8\)), respectively.

Determinations of halogen contents measurable by precipitation titration in sodium chlorite before the decomposition were necessary. Approximately 0.9 g of sodium chlorite was dissolved in 50 mL of pure water, added 1 mL of acetate buffer (pH 4, 1.5 mL of acetic acid and 0.4 g of sodium acetate in 200 mL of pure water) to make the pH value ca. 5, and titrated with the silver(I) solution (ca. 200 mmol kg\(^{-1}\)). The halogen contents were 27.635 % (mass fraction); the SD and RSD of the measurements were 0.792 % and 2.87 % (\(n = 10\)), respectively. Therefore, the corrected assay of sodium chlorite was 79.347 %.

4.4. Measurement uncertainties of sodium chlorite determinations through paths A to C

A summary of the uncertainties of sodium chlorite determinations is given in Table 1. Consequently, the assays (mass fraction) of sodium chlorite were 79.56 % ± 0.51 % (\(k = 2\)), 80.45 % ± 0.51 % (\(k = 2\)) and 79.35 % ± 1.62 % (\(k = 2\)).

There is a statistical treatment, weighted mean, which combines more than one result [10]. A weighted mean is calculated from each weighting value varied inversely with the two power of each uncertainty. A combined assay of sodium chlorite was calculated by a weighted mean of all of three assays: 79.98 % ± 0.35 % (\(k = 2\)).

4.5. Measurement repeatability for solution-form sodium chlorite

The repeatability of two redox titrations for sodium chlorite was around 0.3 %. The repeatability was worse considering those of gravimetric titration methods that typically are less than 0.01 %. There was
a high possibility that the larger measurement deviations for the solid would be caused by the fluctuation of weighing and the samplings due to the hygroscopicity and the inhomogeneity because obtained deviations were less than 0.05% (RSD, \( n = 11 \)) and less than 0.015% (RSD of the mean, \( n = 11 \)) for ‘solution-form’ samples of ca. 1800 ppm and ca. 1300 ppm as sodium chlorite.

### Table 1. Uncertainty budget for sodium chlorite assays.

| Uncertainty source                              | Relative standard uncertainty, % |
|------------------------------------------------|----------------------------------|
|                                                | Path A  | Path B  | Path C  |
| Certified value of CRM                         | 0.0011  | 0.0075  | 0.0235  |
| Repeatability of standardization of titrant    | 0.0040  | 0.0091  | 0.0022  |
| Repeatability of titration of sodium chlorite  | 0.3237  | 0.3151  | 0.1672  |
| Weighing of CRM                                | 0.0023  | 0.0023  | 0.0017  |
| Weighing of sodium chlorite                    | 0.0347  | 0.0347  | 0.0116  |
| Weighing of titrant                            | 0.0005  | 0.0007  | 0.0006  |
| Molar mass of sodium chlorite                  | 0.0030  | 0.0030  | 0.0030  |
| Correction with halides-impurity determinations| ***     | ***     | 0.792   |
| Combined standard uncertainty                  | 0.3257  | 0.3172  | 0.810   |
| Expanded uncertainty (coverage factor \( k = 2 \)) | 0.65    | 0.63    | 1.62    |

### 5. Conclusions

A multipath gravimetric titration technique which is an approach to use three different stoichiometric reactions was performed to assay sodium chlorite in the present paper. All titrimetric procedures using a combination of gravimetric titration and coulometric titration are capable to ensure the traceability of the mass fraction of chlorite ions to the SI. Three different stoichiometric determinations were consistent with each other within their measurement uncertainties. The author has reported the establishment of perchlorate and chlorate standards by performing multipath titration techniques. Employing different stoichiometric reactions has decreased the risk and the contribution of measurement biases of a single method, and is one of the best approaches to obtain more reliable chemical standards.

### References.

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